"REACTIONS OF CHROMIUM (VI) AND COBALT (III) COMPLEXES IN AQUEOUS SOLUTIONS"

by

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A C K N O W L E D G E M E N T S

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A B S T R A C T

The stopped-flow apparatus has been used to study the reactions of chromium (VI) and 12-tungsto - cobaltate (III) anions with sulphur - containing organic ligands in aqueous perchlorate solutions.

The oxidation of thiourea and its N-Substituted derivatives (L) by chromium(VI), $HCrO_4^-$, proceeds via the formation of 1:1 complexes, O_3CrL, which are considered to be sulphur bonded. These intermediates, formed within the time of mixing on the stopped-flow scale have been characterised, and from changes in the initial absorbance, the spectrum and thermodynamic parameters associated with complex formation have been determined. The kinetics of the electron-transfer reactions to yield chromium (III) complexes as products have been investigated, with the principal pathway involving a second-order dependence on the ligand. The significance of this observation is discussed.

The ion $HCrO_4^-$ also oxidises thiols such as penicillamine, glutathione and 2 - mercaptoethylamine via the formation of intermediate sulphur-bonded esters. Unlike the complexes formed with the thioureas, the rates of formation of these esters are sufficiently slow for kinetic measurements to be made using the stopped-flow method. The rate constants for the acid-catalysed formation pathway were found to be smaller than those hitherto reported for similar reactions involving this oxidant. The significance

of these values is discussed and comparison made with other values reported. Second-order dependences of the redox rates on ligand concentrations are also described.

Finally, in order to attempt an evaluation of outer-sphere systems, the reduction of the large 12-tungsto - cobaltate(III) anion by thiourea and its N-substituted derivatives has also been investigated using the stopped-flow technique . No complex formation was detected but some deviation of the rate from first-order ligand dependence at higher ligand concentrations and low temperatures is interpreted in terms of the formation of outer-sphere complexes. Possible mechanisms of the reactions are discussed.

C O N T E N T

GENERAL INTRODUCTION

Up till the early part of this century the detailed chemistry of inorganic reactions in aqueous media was limited to observation of their stoicheiometry. Interpretation usually involved thermodynamic considerations and time dependence was neglected almost entirely. Attainment of equilibrium in some particular systems was regarded as being slow and a judicious choice of catalysts was necessary to increase the rate of reactions. In all other cases, the assumption was made that reactions involving ions occurred rapidly and went to completion.

The simple stoicheiometry of gaseous chemical systems served as the basis for the development of our knowledge of the theory of chemical kinetics. However, the early kineticists found the field of organic chemistry more attractive and only in a few instances were studies made of inorganic reactions in solution. More recently the development of new techniques of kinetic observation has led to a more general study of the solution chemistry of inorganic reactions especially in the area involving the reactions of metal ions.[1-11]

Despite the late upsurge of interest in the kinetic studies of inorganic reactions, the number of systems which could be investigated was also limited. Infact only those reactions with half lives greater than Ca 30s could be studied using the so called 'conventional methods'. However, with the development of fast reaction techniques[12-15] it has

become possible to examine in detail systems which had previously been outside the scope of investigators i.e. with half lives of the order of milliseconds or less.

Fast Reaction Techniques

Although Hartridge and Roughton are now looked upon as the 'founding fathers' of the fast reaction technique (mainly the continuous and to some extent the stopped - flow technique), there are indications from the literature that theirs might have been a development and subsequent application to rapid reactions in solution, of the basic principle applied to gas reactions at an earlier stage by some workers. For example, an application of the flow principle (but without mixing) was made by Ernest Rutherford[16] in 1897 in his measurement of the coefficient of recombination of gaseous ions. In 1905, Raschig[17] made kinetic studies of the rapid reaction between nitric oxide and oxygen by driving the two gases into a T-shaped glass mixer and then, through glass tubing of varying volume, into an absorbing solution which stopped the reaction. The time during which the reaction had proceeded was calculated from the volume rate of gas flow and the volume of intermediary tubing between the mixer and the absorbing solution, This technique was thus a direct precursor of one of the few developed by Hartridge and Roughton called the chemical or "quenching" method. In 1922, Stewart and Edlung[18] drove a mixture of ethylene and bromine vapour into a mixer and then into a reaction tube. By suddenly turning off a stream of mixed

gases, and following the changes in the reaction tube manometrically, the course of the reaction was continuously followed. Although the timing was rather slow, their method is obviously a precursor of the 'stopped-flow' method.

It was in 1923 that Hartridge and Roughton[19,20] developed a method for solution studies which can be used to follow reactions with half lives of the order of (10-0.001)s. The principle of their method was to place the two reactants in separate containers, force them into a special mixing chamber and then through an observation tube. The composition of the streaming fluid was determined at various points along the observation tube by optical, thermal electrical, chemical or other methods of analysis applicable to rapidly moving fluids. This is the continuous flow method in which the rate of flow of the fluid was kept constant.

Another alternative is to follow the extent of reaction at a fixed point about 1cm from the mixing chamber by varying the velocity of fluid flow either in discrete steps as in Millikan's[21] procedure, or continuously as in the accelerated flow method of Chance[22]. Apart from the great advantage of minimal fluid requirement of the latter, it is also capable of measuring half lives of 0.3 milliseconds.

The stopped - flow method is relatively simpler than the continuous flow methods so far discussed. In this method, the two reactants are mixed just as in the continuous flow but the flow of the reacting fluid is suddenly and instantaneously stopped. The progress of the reaction is then

monitored using a fast response device. With the development of rapid electronic monitoring methods over the last few years notably through the work of Chance[22], Gibson[23] and later workers, the stopped - flow method has superseded the continuous - flow methods in importance and regularity of use in the measurement of rapid chemical reactions.

The stopped - flow method has several advantages over the continuous flow method:

a) It is independent of the rate and character of flow down the observation tube

b) a permanent record can be obtained of the progress of the reaction over a period starting at a few milliseconds after mixture and extending as long as desired

c) It is free from the distorting effect of mechanical disturbances

d) the volumes of reagents required are minimal.

This section would be incomplete without a mention of the relaxation techniques which are generally applicable to the study of reversible reactions having half lives as short as 10^{-9}s. In all cases the position of a chemical equilibrium is disturbed by rapid variation of a physical parameter such as temperature, pressure or electric field intensity. In such a situation, there is a time lag while the system approaches the new position of equilibrium and this time lag is related to the rate constants of the forward and back reactions. Eigen[12] has described appropriate

experimental methods and has shown how the observed equilibrium shift can be related to chemical rate constants.

With the development of relaxation techniques, rate constants near the diffusion controlled limit of the order of 10^{10} - 10^{11} $l\ mol^{-1}s^{-1}$ can be measured. This method also has the added advantage of being free of the shortcomings or limitations of the flow methods since it involves only a single mixed solution. However, in view of the considerable difficulties associated with its use for irreversible reactions, the stopped - flow method is generally preferred for reactions both reversible and irreversible where the half lives fall within its time - scale.

For many years the development and subsequent usage of both the continuous and stopped - flow method was dominated by workers with physiological or biochemical interests notably by Roughton[25], Gibson[25] and others working on reactions of haemoglobin and by Chance[26] on enzyme reactions. However, it was not until the late 1950s early 60s that results were published of the kinetic investigations involving metal ion reactions in solution [27,28].

It has been established that such reactions often involved ligand - substitution or electron - transfer or both. In redox reactions between two metal ions or a metal ion and non-metallic substrates, ligand substitution is known to occur and is thought to provide a low - energy pathway for electron transfer. Typical examples of this could be found in the Chromium (Vl) oxidation of both metal and non metallic

substrates[29].

Ligand Substitution Processes

Until relatively recently, mechanistic studies were restricted mainly to the complexes of Cr^{III}, Co^{III}, Pt^{II} and Pd^{II} which undergo substitution slowly and which may be investigated by use of conventional techniques. Taube[30] infact pointed out in 1952 that metal ion complexes can be divided roughly into two categories basing the division on the kinetic data available at that time. Those whose reactions are complete within the time of mixing (one minute, room temperature, about 0.1M solutions) were classified as labile while those that react at rates too slow to measure or at rates that can be followed by conventional techniques were called 'inert' complexes. However, recent application of rapid reaction techniques to the study of labile complexes has not only widened the scope of the ligand substitution reactions that can be and are being studied but has in effect helped to extend our knowledge in this field.

The most general form of the ligand substitution reactions is given in equation (2)

$$MX_n + Y \rightleftharpoons MX_{n-1}Y + X \qquad (2)$$

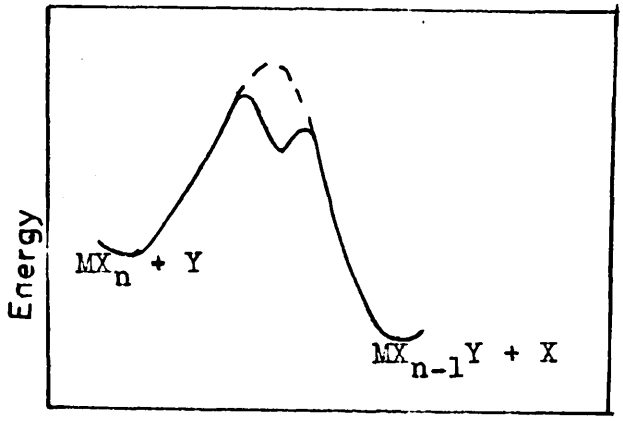
Studies generally involve complex formation reactions and interpretation of the results requires a knowledge of the structure of solvated metal ions together with the lability of its associated solvent molecules. These data are

available for a substantial number of ions[31] although the exact nature of many is still uncertain. The bulk of the studies carried out in this field have been performed in aqueous solution, and the reaction in most cases refers to the replacement of solvent water in the co-ordination sphere of the metal ion by the ligand.

Metal ion complexes are of two general types, outer sphere and inner sphere. In an outer sphere complex in solution, the primary co-ordination sphere of the metal ion is said to be intact whereas the co-ordination sphere of the inner sphere complex is penetrated by the ligand to form a bond. The existence of outer sphere complexes in solution was first recognised by Bjerrum[32] and the participation of these outer sphere complexes (ion pair formation) as intermediates in the formation of inner-sphere complexes has been considered for sometime[33]. Thermodynamic and kinetic studies of the slowly reacting Cobalt (III) and Chromium (III) Complexes [33,34] indicate active participation of outer-sphere complexes. With the development of modern techniques for the study of very rapid reactions, the role of outer sphere complexes in the reactions of labile metal complexes and their general importance in complex formation reactions have also been established [35-38].

Substitution reactions in general involve both breaking and making of metal ion ligand bonds. The mechanistic aspects have been discussed previously [1-11], for inorganic

complexes the nomenclature used for describing the different modes of reaction has been introduced by Langford and Gray[6]. Four categories are distinguished: A (associative), D (dissociative), Ia and Id the last two being described as interchange with predominantly associative or dissociative character respectively. The energy profile diagram which illustrates these mechanisms has the form shown in Fig. 1.



Potential energy curves for substitution reactions

$MXn + Y \rightleftharpoons MX_{n-1}\ Y + X$

FIG I

The dotted curve represents a concerted reaction and corresponds to interchange. The full line represents either an association or dissociation mechanism depending on whether the intermediates are MX_nY or $(MX_{n-1} + X + Y)$ respectively. The three types are represented by equations in the following way:

$MX_n + Y \rightleftharpoons MX_nY \rightleftharpoons MX_{n-1}Y + X$ associative

$MX_n + Y \rightleftharpoons MX_{n-1} + X + Y \rightleftharpoons MX_{n-1}Y + X$ dissociative

$MX_n + Y \rightleftharpoons X\text{---}MX_{n-1}\text{---}Y$ interchange

An examination of Fig 1 shows that for a dissociative process, the entering group does not interact directly with the reaction centre in the transition state, whereas for the associative process there is bonding. It is therefore possible to distinguish between these two mechanisms experimentally. In an Id (dissociatively activated) intimate mechanism, bond breaking provides a greater contribution to the activation energy than bond making, the rate of reaction should therefore be relatively insensitive to the nature of the entering group, while the rate of an Ia mechanism should be very sensitive to the entering group because of the greater contribution of bond making to the activation energy. It is generally more difficult to distinguish between D and Id and between A and Ia than it is to distinguish between Id and Ia. Distinction between the former is based purely on the life time of the intermediate and activated complex.

It is often possible to assign a mechanism on the basis of the rate law and product analysis. In the anation reactions of $Co(CN)_5H_2O^{2-}$ (ref 39) and $Co(NH_3)_5H_2O^{3+}$ (ref 40) the D mechanism has been shown to be operating with the existence of the species $Co(CN)_5^{2-}$ and $Co(NH_3)_5^{3+}$ as intermediates. Confirmation of their existence as discrete species has been postulated by their selective

reactivity towards various nucleophiles. Reactions of the type

$$Co(NH_3)_4 SO_3 (X)^{n+} + Y \longrightarrow Co(NH_3)_4 SO_3 (Y)^{n+} + X \qquad (3)$$

where X = NH_3 , OH^-, NO_2 or NCS^- and Y = OH^-, CN^-, NO_2 or NCS^- are all thought to proceed via a mechanism involving the common intermediate $Co(NH_3)_4 SO_3^+$ (ref 41 and 42).

As far as the A mechanism goes, no unequivocal example of this type of reaction is known for octahedral complexes[1] but in the reaction of the square planar Rh (I) species with amines, there is strong evidence for the formation of a five - co-ordinate intermediate.[43] This has also been found in the reaction of Pt (II) with cyanide.[44]

The Complexation of Labile Metal - ions

Mostly through the work of Eigen[45] and his co-workers using relaxation methods, the relative rates of attachment of a ligand to one of these metal ions are now available. In the interpretation of the results obtained, the mechanisms in general reflect the reaction types for inert species.

For ions of the alkali metals e.g. Li^+, Na^+, K^+, Rb^+ and Cs^+ and alkaline - earth metals like Ca^{2+}, Sr^{2+} and Ba^{2+} (except Be^{2+} and Mg^{2+}) the rate constants for loss of water are not only quite high ($>10^7$ S^{-1}) with all the ligands used but there is also some variation from one ligand to the other. This is an indication not only that water molecules are lost from the co-ordination sphere of the metal ions with relative ease, signifying fast exchange with the solvent, but also

that the rate determining step is most likely to be the attachment of the ligand. In each group the rate increases with the size of the ion, though by less than a power of ten. This variation in rate from one ion to the other is attributable to the differences in the size/charge ratio of the ions which measures their electrostatic attraction for ligand dipoles.

With the alkali metals, complexes are formed only with strongly interacting agents which are capable of forming chelate complexes such as EDTA, nitrilotriacetate etc. and the rates which were found to be very high were measured by the ultrasonic absorption method.[45] For the alkaline earth metals rate constants with such chelating agents[36,45] are of the order of $(10^7 - 10^9)$ l $mol^{-1} s^{-1}$ which is the same as that for calcium ions with sulphate.[35,37]

Zn^{2+}, Cd^{2+} and Hg^{2+} which are all d^{10} ions react about as fast as Ca^{2+} but do not show marked differences between ligands. Examples of this could be found in the reactions of Cd^{2+} with bromide ion[46] and with EDTA[47] both of which have rate constants about 10^9 l mol^{-1} s^{-1}. From the results obtained for this group of ions one might be tempted to postulate an Ia rather than an Id mechanism for the complexation reactions.

A second group of cations to be considered are those for which the rate constants are less than 10^7 S^{-1} and practically independent of the nature of the ligand. This

group includes Mg^{2+}, most of the divalent ions of the first series of transition elements and some of the trivalent rare earth cations for the reaction of Mg^{2+} with SO_4^{2-}, $S_2O_8^{2-}$ and CrO_4^{2-} (ref 35,37) and with adenosine di- and triphosphate[36] a rate constant of about 10^5 S^{-1} has been obtained in all cases. This is an indication that the rate determining step is largely independent of the nature of the ligand and is therefore likely to be the removal of water from the co-ordination shell of the cation. The mechanism proposed by Eigen[36] for this group of ions involves the formation of an outer-sphere complex at rates in the region of diffusion-controlled processes, followed by a dissociative ligand interchange.

The small increase in rates with increase in the size of the metal ion in the case of rare earth elements was explained on the basis of electrostatic effects. This type of explanation however breaks down for the transition - metal series - Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. The slow rates shown by Ni^{2+} and V^{2+} probably result from crystal field stabilisation of the transition state[1] while the high rates of Cr^{2+} and especially Cu^{2+} have been attributed to John - Teller distortion of the octahedral structure. In these cases the axial water molecules are held less rigidly than those in the equatorial positions and exchange can take place more rapidly with the solvent.

In anation reactions involving a third group of metal

ions M^{n+}, the general intimate mechanism operating for these cations is far from resolution. Unlike the first two groups considered above, the rate of hydrolysis of these cations is greater than the rate of water loss from the co-ordination sphere of the ion. Consequently they often react through their hydrolysis products. Kinetic evidence of such parallel reactions is often obtained for complexation by anions of strong acids with the observed rate constant, k_{obs}, being of the form $k_{obs} = k_1 + k_2/[H^+]$ the latter term being interpreted as resulting from the reaction of $MOH^{(n-1)+}$.[48]

Consequently reduction in charge upon hydrolysis leads to a more facile loss of water by such species with the result that they exhibit kinetic behaviour similar to that of the second group. Examples of such cations are Fe^{3+} (ref 49), Al^{3+} (ref 50) and Be^{2+} (ref 51).

Evidence for some degree of associative character exists for the largest ions of this group such as $Rh(NH_3)_5 H_2O^{3+}$ [52] and also for ions in this group which are of moderate size with fewer than three d electrons, such as V^{3+} [53,54].

Fe(III) is the most widely studied of this group and the rate constants for the reaction of this cation with various anions show a broad parallelism with the basicity of the anion.[49] This could, of course, be interpreted as indicating some associative character in the intimate mechanism. Eigen[36] proposed an alternative explanation

wherein the outer sphere complex formed between the cation and the ligand breaks up under the influence of both to give $FeOH^{2+}$ and HL, which then react in a dissociative manner. The overall substitution rate is thus governed by the extent of hydrolysis. This mechanism was however criticised[6] on the basis that the anation rate constants of $Cr(H_2O)^{3+}$ which also undergoes hydrolysis much more rapidly than it loses water, was found to be insensitive to ligand basicity.

Seewald and Sutin[55] pointed out that proton ambiguity associated with this acid independent path does not allow distinction to be made between routes (4) and (5).

$$Fe(H_2O)_6^{3+} + L^- \rightleftharpoons Fe(H_2O)_6^{3+} \cdot L^- \rightleftharpoons Fe(H_2O)_5L + H_2O \qquad (4)$$

$$Fe(H_2O)_5OH^{2+} + HL \rightleftharpoons Fe(H_2O)_5OH^{2+} \cdot HL \rightleftharpoons Fe(H_2O)_5L + H_2O \qquad (5)$$

From the kinetic data available the range of anation rate constants associated with Fe^{3+} and $FeOH^{2+}$ lie between 4 and 127 l $mol^{-1}s^{-1}$ for the former and 3×10^3 to 3×10^5 l $mol^{-1}s^{-1}$ for the latter. The first order rate constant for water exchange for Fe^{3+} is 150 s^{-1}, while that for $FeOH^{2+}$ has been estimated as 10^4 s^{-1} (ref 56). These relatively small trends in rate constants with varying ligands have been attributed to the variations in the magnitudes of the outer sphere complex formation constants.[57] If this interpretation is valid, it would appear that bond breaking is the dominant feature of ligand incorporation into the inner co-ordination sphere of both iron(III) species.

Electron transfer Reactions

The stability and reactivity of an ion in any oxidation state is known to be influenced by the presence of ligands. Infact a particular oxidation state of a metal ion is said to be stable only when the redox involves an unfavourable free energy change or the activation energies are too large.[5,58]

The electron transfer process itself must satisfy the Franck - Condon restrictions which arise in principle from the fact that the act of electron transfer takes place within a time that is very much shorter than the time required for nuclei to change their positions. In order words, nuclear motion is slow as compared to electronic motion and the former can be regarded as stationary during the time taken for electron transfer. Two important consequences of this principle are that (a) both the oxidant and the reductant must undergo reorganization before electron transfer in a way that ensures that their energies in the transition states are identical. This minimises the energy change on electron transfer. The second is that restrictions are placed on changes in spin angular momentum. Spin inversion when it occurs is found to inhibit the overall redox rate. The electron transfer reaction between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$ is a typical example of this effect where the rate is found to be very slow.[9]

In addition to the contributions from the two sources outlined above, the activation energy will also contain terms

resulting from the coming together of charged species and the necessary rearrangement of the solvation shells. Marcus, Zwolinski and Eyring[59] have derived a theory for electron transfer reactions based on the hypothesis that the mechanism involves electron tunnelling. In terms of the transition state theory of chemical kinetics, their results may be written in the form

$$k = \frac{KT}{h} K^1 \exp\left(-\frac{\Delta G_r}{RT} \quad -\frac{\Delta G^*_e}{RT} \right) \qquad (7)$$

where K^1 is a transmission coefficient which includes the probability of barrier penetration. ΔG^*_e is the activation free energy for overcoming electric repulsion between the ions and ΔG^*_r is the activation free - energy for rearrangement of the hydration and co-ordination shells. The transmission coefficient, which is always less than one, increases (tending to increase the rate constant) as the exchanging partners come closer together. Because of electro-static repulsion, the energy of activation also increases and this tends to decrease the rate. However, at an optimum distance a maximum exchange rate is obtained. Similar theories for electron transfer by a tunneling mechanism have been proposed by Weiss[60] and by Marcus.[61]

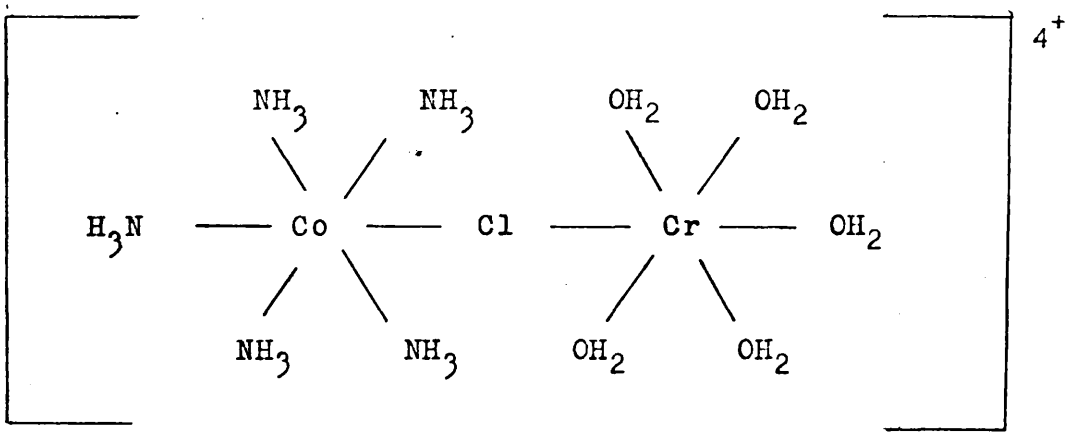
Electron-transfer reactions in solution have been divided into two groups depending on whether they proceed by way of an outer sphere or inner sphere activated complex.[62] In the outer sphere activated complex, the interaction between the oxidant and the reductant at the time of electron

transfer is small and the reaction takes place with their co-ordination shells intact. In the inner sphere activated complex, both the oxidant and the reductant are firmly bonded during the electron transfer through at least a ligand common to both co-ordination shells in the case of two metal ions. The equivalent transition state involving a metal ion and a reducing ligand corresponds in structure to the stable inner sphere complexes discussed earlier.[58a] In some cases detectable intermediates are formed from both types of inner sphere activated complex.[63-65] The question of intermediates in oxidation reactions has been discussed in detail by Halpern.[66]

Electron exchange reactions between MnO_4^- - and MnO_4^{2-} has been studied by Sheppard and Wahl and found to proceed by an outer sphere mechanism,[67] so also is the exchange between substitution inert $Co(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{2+}$ because co-ordinated ligands such as ammonia and ethylenediamine cannot form bridges even though Cr(II) is labile. However, on replacing one of the six ammonia groups co-ordinated to Co^{III} by a chloride ion, the same reaction was shown by Taube[68] to proceed by an inner sphere mechanism. The reaction in acid solution is

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_3O^+ \longrightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_4^+ \qquad (8)$$

and the activated complex presumably has the structure



For the complexes $[Co(NH_3)_5L]^{3+}$, a survey of the ligands L which act in the same manner as Cl^- has been made.[69] Transfer to Chromium is observed with F^-, Br^-, I^-, SO_4^{2-} N_3^-, NCS^-, carboxylate ions, PO_4^{3-}, $P_2O_7^{4-}$ and OH^-. After electron transfer the initially labile complex may be inert to substitution.

In many instances, the oxidations of ligands by metal ions have been known to proceed by an inner sphere type of mechanism with the involvement in some cases of well - characterised intermediates.[64,65,70] Inner-sphere complex formation of the type

$$MX_n^{a+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX_{n-1}L^{a+} \longrightarrow M^{(a-1)+} + P$$

is probable where the substrate involved is a neutral or negatively charged species. If a transient complex ion is formed in the course of any redox reaction, there are three possible rate controlling factors:

(a) the rate of formation of the intermediate

(b) the rate of electron transfer within the complex

ion and

(c) the rate of breakdown of the complex.

If (a) is rate determining, the factors governing this step or steps have been discussed earlier. If (b) is the case, in the absence of spin inversion effects the rate of reaction is expected to bear some relationship with the electron affinities of the ligands. If breakdown of the complex is the rate controlling factor, then the strength of the bond will become important.

Detection of the intermediate depends on the relative values of the rate constants k_1, k_{-1} and k_2. This will be achieved, (a) if k_1 and k_{-1} are very much greater than k_2 with $k_1 \geq k_{-1}$. In this case, if the rate of redox reaction falls within the stopped-flow range then the formation of the complex preceding this step may be instantaneous. (b) if $k_1 < k_{-1} > k_2$, complex formation and disappearance may both be observed. (c) if $MX_{n-1}L$ is maintained at a small steady state concentration the observed rate constant will be a function of k_1, k_{-1} and k_2. (d) if $k_2 \gg k_1$, then the observed rate constant for the redox reaction is controlled by k_1 and this corresponds to the case where complex formation is the rate determining step. Many metal ion oxidations of ligands are believed to be of this type.[71]

Although complex formation between oxidant and reductant may be detected this does not automatically mean that this species plays a direct role in redox process.[66] There is a

kinetic ambiguity which does not allow distinction to be made solely on the basis of the observed rate law, between whether or not the complex is a true intermediate. If however, such an entity is formed in measurable concentrations the establishment of the existence of a sequential process may be made spectrophotometrically, especially by the observation of induction periods and isosbestic points.

CHAPTER 1

EXPERIMENTAL METHODS

The Stopped - Flow Method

Virtually all the stopped - flow apparatus in use today developed from that first designed by Roughton.[72] In constructing an efficient stopped - flow apparatus, several points must be taken into consideration.

(a) The reactant solutions must be thoroughly and rapidly mixed. The mixing chamber must therefore be properly designed to take care of these two requirements.

(b) The flow velocity must be adequate i.e. above critical velocity for turbulent flow. The critical velocity is given by Reynolds formula [24]

$$U_c = \frac{N_R \eta}{\rho d}$$

where η is the viscosity of the fluid in poise, ρ, the density and d, the diameter of the tube in cm. N_R is known as Reynolds number and is about 2000 for fairly short tubes.

(c) The observation point should be some millimeters from the mixing chamber, to ensure that mixing is complete before observation. However it should not be too far away since the lost time between mixing and observation must be minimised.

(d) Finally, the flow must be stopped very quickly for the efficiency of mixing falls if the flow is too slow. Moreover, the more sudden the

stoppage the greater the chances of faster reactions being observed.

The sophistication of the apparatus depends on the lifetime of the reaction it is capeble of measuring.

Two types of stopped - flow devices (three in all) were available and are now described in detail. The first type (A and A^1), the diagram of which is provided in Fig 1.1 was used for reactions with half-lives of 0.05 - 5s whereas a modified version (B) in Fig 1.4, was used for all other reactions with half lives greater than 10s.

In the 'rapid' flow system (A) and (A^1), the reactant solutions were first introduced into two 10ml glass storage or reservoir syringes and from there transferred to the 2ml delivery syringes by means of two three way taps. The connection of the reservoir syringes to the three way taps was achieved by the use of short lengths of 'Portex' plastic tubing. Solution was transferred to the mixing device by way of glass tubing of 5mm internal diameter. This was achieved by applying the appropriate pressure on the pushing block. The teflon plungers attached to the pushing block forced the solution in each of the two delivery syringes into the glass tubing and hence into the mixing chamber. Plaster of Paris was used to hold the mixing chamber firmly in position to prevent any movement while the plungers were being driven.

The mixing chamber used was a teflon two - stage

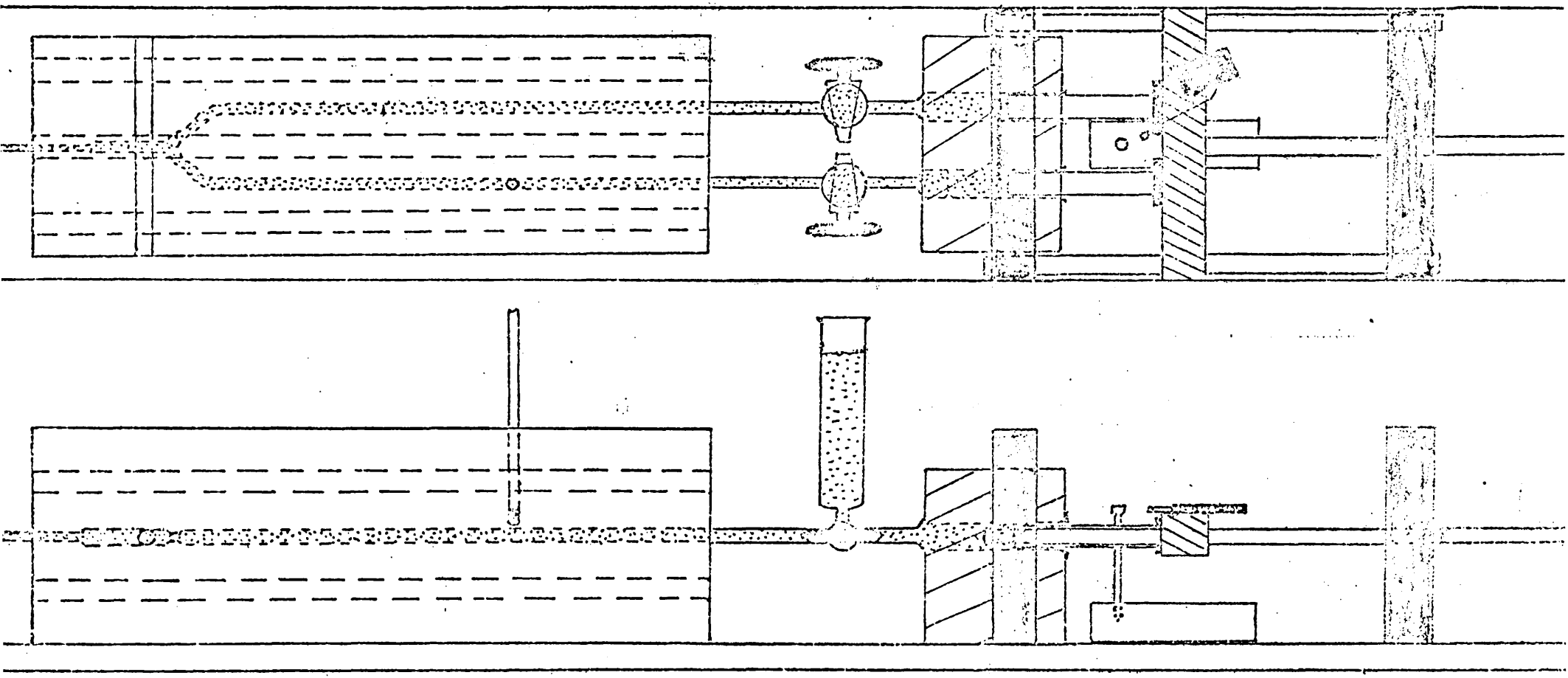


Fig. 1.1.

"Fast" Stopped-Flow Apparatus

1 cm = 1 inch

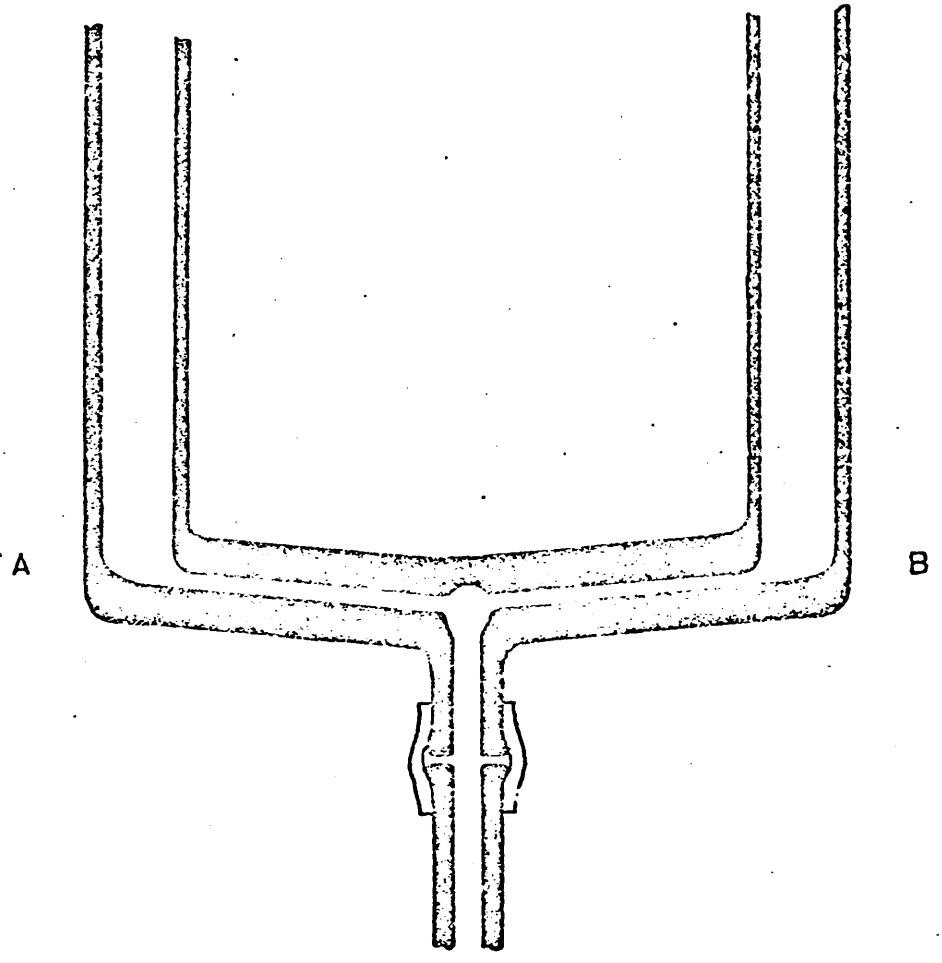
Top :- Plan View; Bottom :- Side View

eight-jet device modified from the original design of Dulz and Sutin.[73] A 'spectrosil' type 134 QS flow - through spectrophotometer cell was attached to the observation tube very close to its exit from the mixer. This cell of 5mm path length had a rectangular cross section. Another stopped - flow apparatus (A^1) was constructed which was virtually identical with the one above but for the material used for the mixing chamber. In this case the material used was perspex.

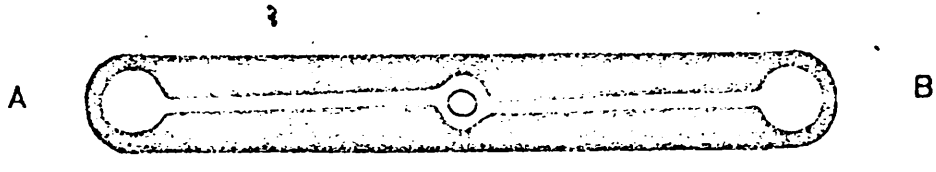
When some minor leakage was observed in the two mixing chambers they were replaced by an all - glass - two - jet mixer of the type shown in fig 1.2. Reaction rates on both stopped flow devices were found to be identical indicating that the mixing efficiency of the two - jet device was just as good as the eight - jet one.

As was pointed out earlier on, effective stopping of the flow is as important as efficient and thorough mixing. This was achieved when the pushing block driven under pressure from a compressed gas encountered a vertical iron pin which was placed in one of several available holes in a brass block. This front - stopping method was used in preference to the conventional back - stopping system as it was found to lessen the recoil which occurred when flow was stopped. Also, it provided greater operational flexibility in that by having a number of holes in series in the stopping pin holder, it was possible to obtain several pushes without refilling the drive-syringes.

Fig. 1.2.



PLAN



SECTION

ALL GLASS TWO JET TANGENTIAL MIXER

Fig. 1.3.

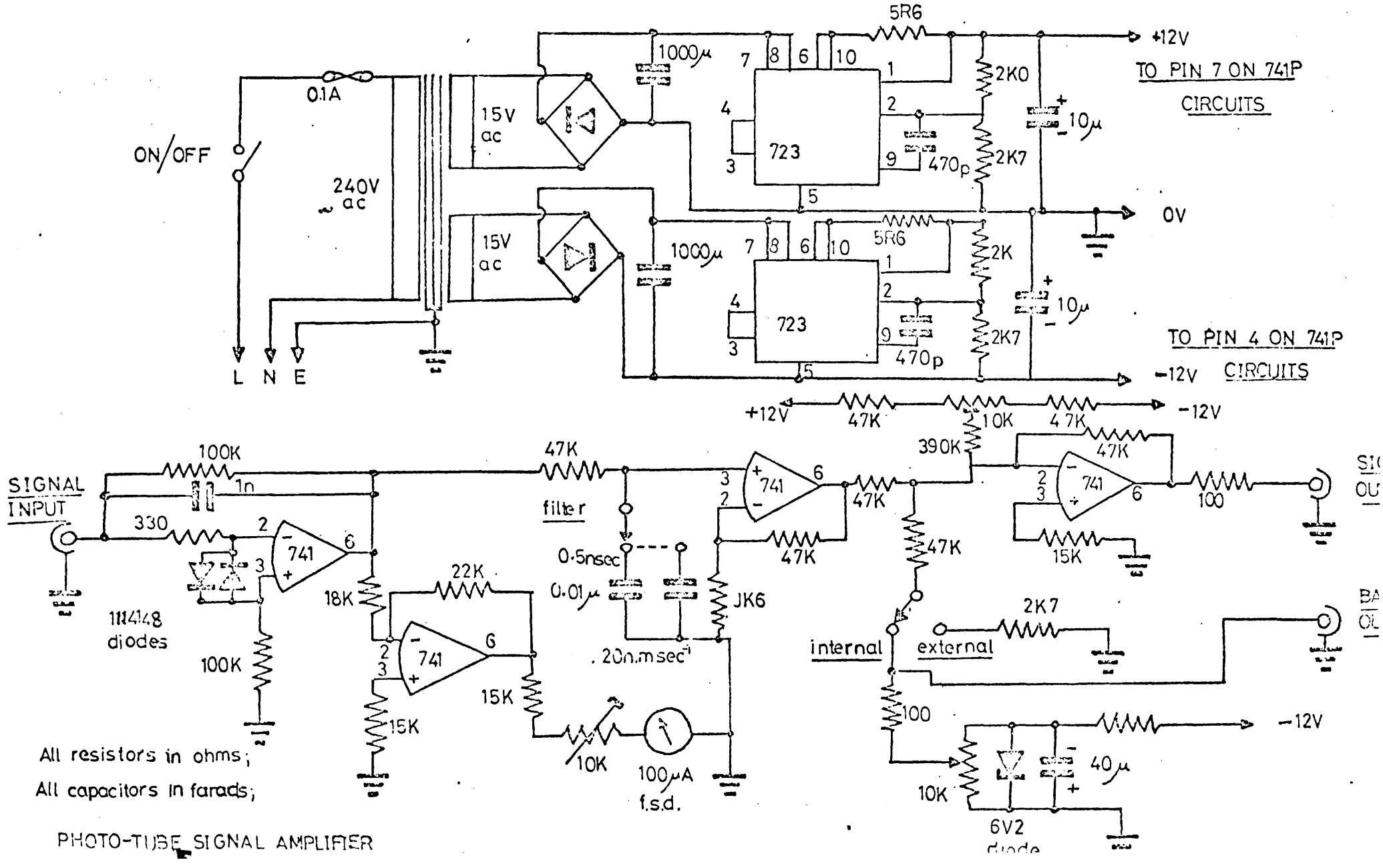


PHOTO-TUBE SIGNAL AMPLIFIER

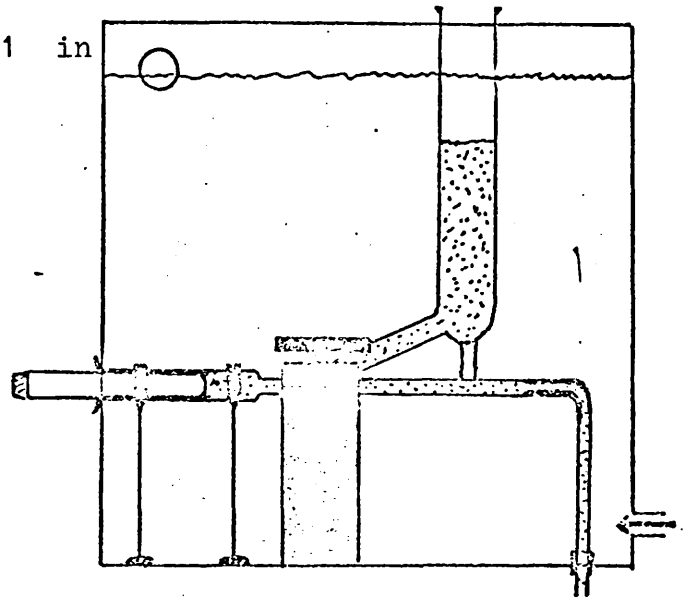
Fig. 1.4.

"Slow" Stopped-Flow Apparatus

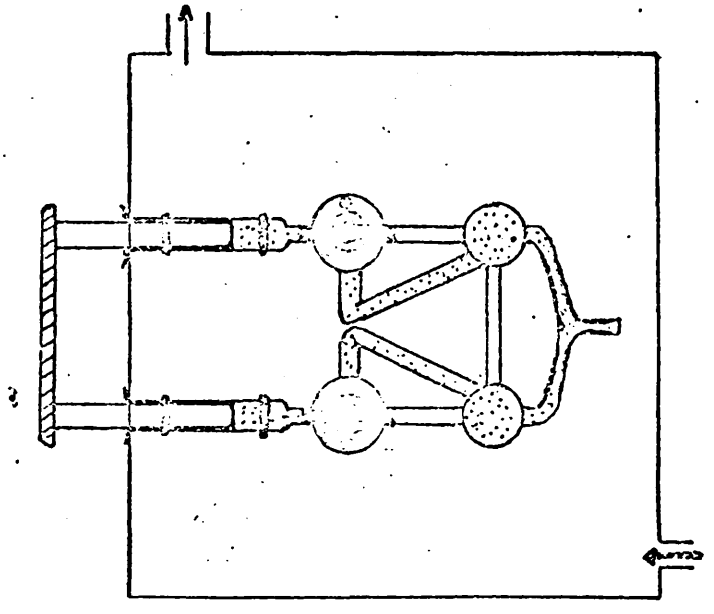
I Side View

II Plan View

1 cm = 1 in



I



II

Thermostatting of solutions was achieved by incorporation of the feed tubes, mixing chamber and observation cell all within a two piece aluminium block through which water was circulated. The heating and circulation of the water from a tank was performed by a Circotherm MKII thermostat. Cooling of the water in the tank was achieved using a 'Tecam' dip-cooler refrigeration unit. The final steady temperature (to $\pm$ 0.1^{o}C) was recorded by a thermometer placed in a cavity in the top block. The bulb of this thermometer was in direct contact with one of the feed tubes and thermal contact between the flow system, the thermometer and the aluminium block was achieved by packing with brass filings.

Photoelectric photometry was used mainly as the method of detection. The power supplies and other electronic equipment were operated from the mains via a type BTR-5 A.C. automatic voltage stabiliser with an output of 240v at 50H$_{z}$.

One of the stopped - flow devices (A) above used an S.P. 500 monochromator (Pye Unican Ltd, Cambridge) as its light source. Visible radiation was provided by a tungsten lamp which was operated at 36 watts (6 volts, 6 amps) from a Unicam 115D power pack. Ultraviolet radiation was supplied by a deuterium lamp which utilised the standard Unicam power unit. The intensity of light leaving the spectrophotometer cell, which was masked to construct an aperture approximately one millimeter square, was monitored using an E.M.I. 6256s photomultiplier tube. Its operating voltage was supplied by an A.E.I. type R1184 power unit. The output of the photomultiplier tube was fed by way of a D.C. amplifier into one input of a Tektronix 2A63 differential amplifier which was

incorporated in a Tektronix 564 storage oscilloscope. The D.C. amplifier circuit contained a number of resistor - capacitor filters. Selection of a particular filter for any run was governed by a consideration of the magnitude of the time constant of the capacitor compared with the half life of the reaction. The other D.C. input signal to the oscilloscope differential amplifier was also provided by the D.C. amplifier circuit . This current could be varied by means of a calibrated helipot and enabled input of a 'backing off' voltage.

Current in the triggering circuit was drawn from the calibration voltage output of the oscilloscope to one terminal of a miniature roller microswitch which was mounted on top of the pushing block. The other terminal was connected to the external trigger input of the 2B 67 Tektronix time base Triggering of the oscilloscope sweep took place when the microswitch was closed as it passed the stopping - pin shortly before flow stopped. Oscilloscope traces were photographed using a Shackman super seven MK II Oscilloscope camera fitted with a polaroid CB-40 land back.

The other stopped - flow apparatus (A^1) of similar design used as its light source a modified Hilger 'Uvispec' monochromator containing a 100 watt Osram tugsten lamp (6.6 amps, 15 volts). Here the power pack was a Farnell stabilised voltage/current S-Series type 15/106L unit. A glass lens was used to concentrate light on the cell. This

limited this apparatus to operation in only the visible region of the spectrum. A Tektronix 5103N single beam storage oscilloscope was used in conjuction with a Tektronix 5A 20N differential amplifier and Tektronix BB10N time base. Traces were photographed with a Tektronix C-5 oscilloscope camera using type 107 polaroid film.

The second type of stopped - flow apparatus (B) which was used for slow reactions with half lives greater than 10s is shown in Fig 1.4.

In this case, both the drive and reservoir syringes together with the mixing device of the type shown in Fig 1.2 were all thermostatted within a large plexiglass tank through which was circulated water from a second larger tank by means of a B.T.L. circotherm heater pump. Temperature control within the latter tank was achieved using the same system as for the first unit already described. Each of the two 10ml capacity pyrex-glass drive syringes was fitted with a specially constructed teflon plungers and connected to a three way teflon-barrelled stockcock by short lengths of 'Portex' surgical tubing. The three way taps were situated as shown in the diagram (Fig 1.4) and supported by perspex pillars. The plexiglass tank was situated directly above a Unicam S.P.800 D spectrophotometer fitted with an S.P. 820 series constant wavenumber scan control and S.P. 850 scale expansion unit linked to a servoscribe chart recorder. The reacting solution passed through the glass tube bent at

right angles downwards to a flow-through cell in the SP 800 housing. This quartz cell had a 10mm optical path-length (Hellma QS 130).

Thermostatting of the solution in the cell was achieved by passage of water through the hollow cell-holder using the circotherm heater - pump. The temperatures of both tanks and that coming from the cell holder were constantly monitored using three thermometers and were found to agree within $\pm$ 0.2^{o}C.

The operation of this stopped flow device (B) is similar to those of type (A) The only difference is that the pushing block in the former case is operated manually instead of using the compressed gas and the optical density change with time is recorded directly by the chart recorder instead of voltage.

Calculation of Results

To analyse the results obtained from the two 'fast' stopped flow apparatus (A and A^{1}) it was necessary to convert the oscilloscope displays of voltage as a function of time to the equivalent absorbance data.

If I_o is the intensity of light transmitted by an optically clear solution (usually water) and I_t is the intensity of light transmitted by a solution of absorbance OD_t at time t then,

$$OD_t = \log_{10} \frac{I_o}{I_t} \qquad (1)$$

For a calibrated photomultiplier tube where the output

current, i, is linearly proportional to the intensity of incident light,

$$OD_t = \log_{10} \frac{I_o}{I_t} = \log_{10} \frac{V_o}{V_t} \qquad (2)$$

Since the impedance of the system is constant.

Calibration of the helipot control is achieved by plotting its voltage output as measured on the oscilloscope screen against the corresponding readings on the control knob (see Fig 1.5). The slope of such plot was found to be 0.005575. The principle is to apply a signal from the back off source which would exactly balance the signal from the photo multiplier tube (P.M.T.). The VBO line would now be in position 0 which represents zero volts of P.M.T. signal when no backing off was applied (see Fig. 1.6). With $V_{B.O}$ now as the reference voltage, the P.M.T. voltage V_t corresponding to any other horizontal line on the screen could be obtained by adding or subtracting the appropriate voltage ΔV. The latter value is given by multiplying ΔR the vertical distance of separation by the oscilloscope gain setting.

This procedure can be illustrated by choosing a hypothetical first-order trace shown in Fig. 1.7 for such a reaction,

$$\log_e \frac{OD_\infty - OD_o}{OD_\infty - OD_t} = k_{obs}\, t \qquad (3)$$

and the pseudo - first - order rate constant, k_{obs}, can be obtained by simply evaluating the slope of a plot of

Fig. 1.5.

Calibration of Helipot Control

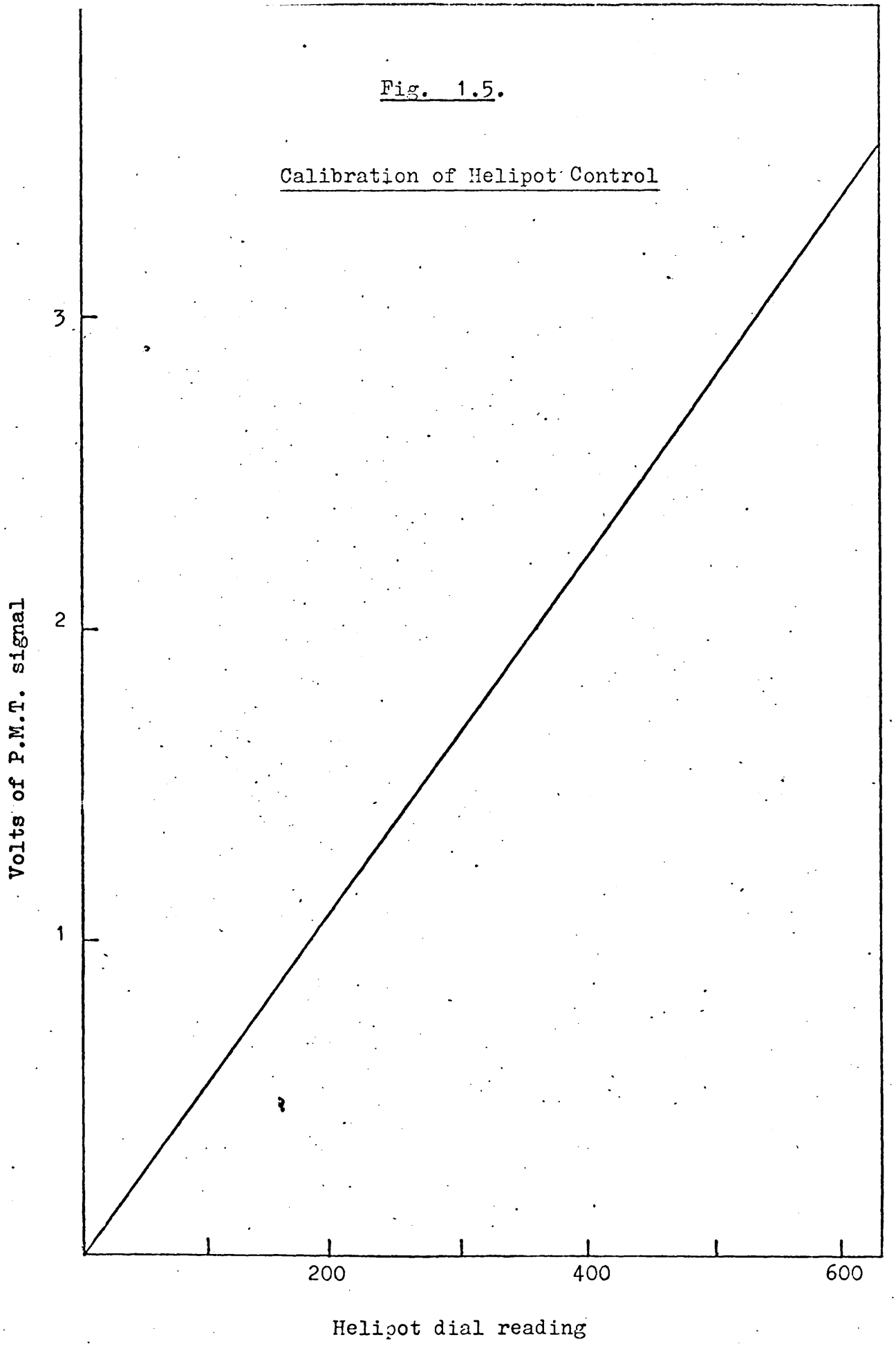
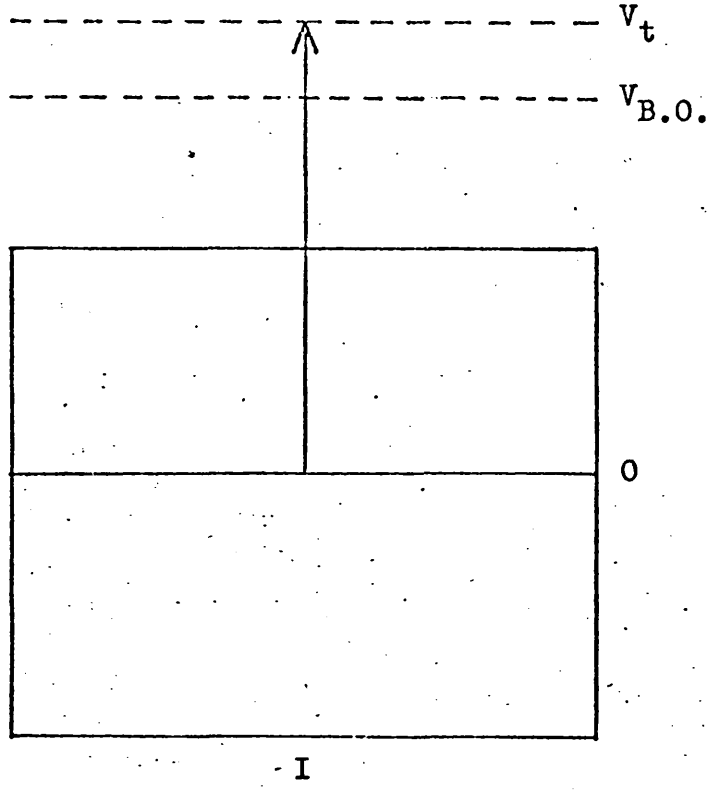


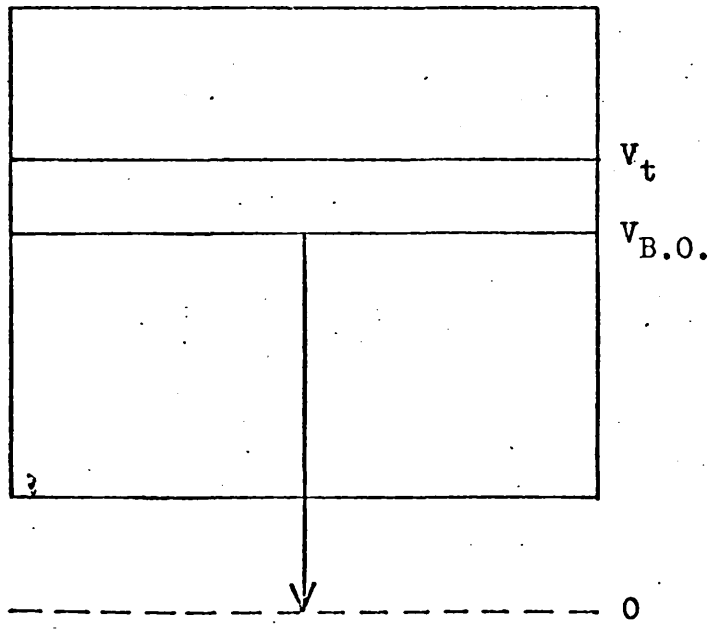
Fig. 1.6.

The Use of the "Back-Off" Helipot



I

V_t volts of P.M.T. signal applied

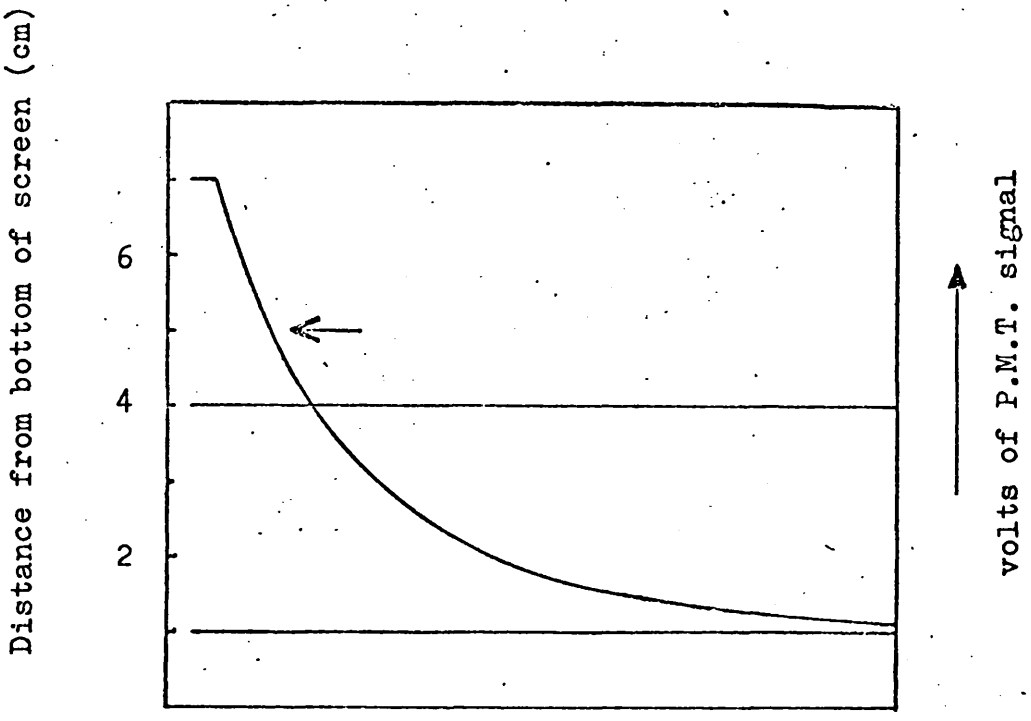


II

$V_{B.O.}$ volts of helipot signal applied in opposite direction to "back-off" most of P.M.T. signal.

Fig. 1.7.

Hypothetical Oscilloscope Trace Representing an Absorbance Increase



Helipot dial reading = 540 ; Gain = 0·10

The horizontal line at 4 cm represents the zero setting of the oscilloscope i.e. the display obtained in the absence of any applied signal.

$\log_e$ (OD∞ - ODt) against time.

$$OD_\infty - OD_t = \log_{10} \frac{I_o}{I_\infty} - \log_{10} \frac{I_o}{I_t}$$

$$= \log_{10} \frac{I_t}{I_\infty}$$

$$= \log_{10} \frac{V_t}{V_\infty}$$

$$= \log_{10} V_t - \log_{10} V_\infty \qquad (4)$$

$$V_{BO} = B.O. \times 0.005575$$

$$= 540 \times 0.005575$$

$$= 3.0 \text{ volts}$$

The voltage corresponding to the bottom of the oscilloscope screen i.e. zero cm., V_z, is calculated by equation (5)

$$V_z = V_{BO} - \Delta V_{BO} \qquad (5)$$

$$\Delta V_{BO} = R_{BO} \times \text{Gain} \qquad (6)$$

$$= 4.00 \times 0.10$$

$$= 0.40 \text{ volts}$$

$$V_z = 2.60 \text{ volts}$$

$$\Delta V_\infty = R_\infty \times \text{Gain} \qquad (7)$$

$$= 1.00 \times 0.10$$

$$= 0.10 \text{ volts}$$

$$V_\infty = V_z + \Delta V_\infty \qquad (8)$$

$$= 2.70 \text{ volts}$$

$$\Delta V_t = R_t \times \text{gain} \qquad (9)$$

$$= 5.00 \times 0.10$$

$$= 0.50 \text{ volts}$$

$$V_t = 3.10 \text{ volts}$$

$$\log_{10} V_t - \log_{10} V_\infty = 0.0600$$

$$\therefore \quad \log_e (OD_\infty - OD_t) = -2.81$$

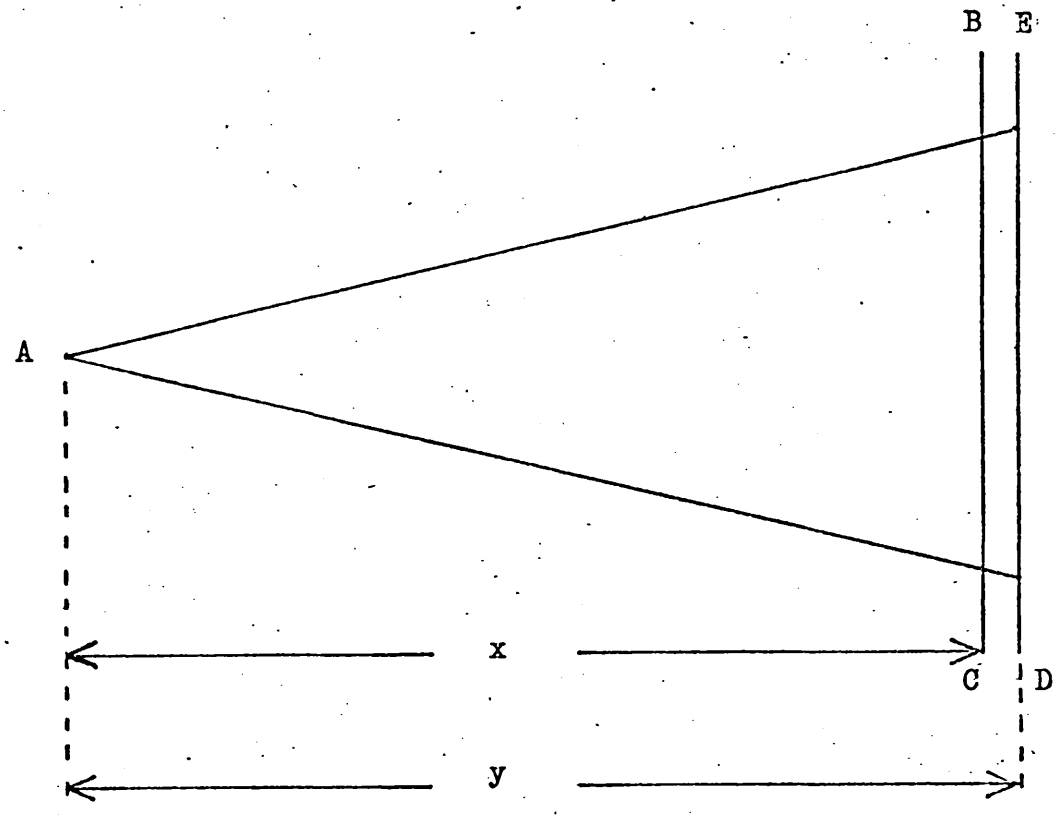
Account was taken of the parallax error when evaluating the various values of ΔV. This is an error which arose from the graticule being fractionally closer to the lens of the camera than was the screen (see Fig 1.8) for the Tektronix 564 oscilloscope used, the various distances R_t measured from photographs of traces were multiplied by 1.032 to get the actual distance on the screen. A programme was written for a Nova 1200 computer (see appendix 1) which converted transmission data into optical density changes and also gave values of $\log_e (OD_\infty - OD_t)$ at any time t.

The mixing ratios of the stopped - flow systems were determined by pushing dilute solution of ferroin, $Fe(phen)_3^{2+}$, against water. With the ferroin in one reservoir, water in the other and vice - versa, the resultant optical density obtained in each case was compared and also with that obtained when the same concentration of ferroin was driven through. The results indicated a ratio of 1:1 within an experimental error of $< 1\%$.

The dead times of the two apparatus were determined by monitoring the complex formation reaction between Fe^{3+} and NH_4NCS in 0.2M $HClO_4$ at λ = 465nm. The reaction carried out in excess iron (III) was found to be pseudo - first order[74] and the dead time is the time through which it was necessary to extrapolate a plot of log (OD_∞ - ODt) versus time to the value corresponding to log (ODo) (see Fig 1.9). The latter

Fig. 1.8.

Illustration of the manner in which error can arise as a result of the graticule not being in the same plane as the oscilloscope display.



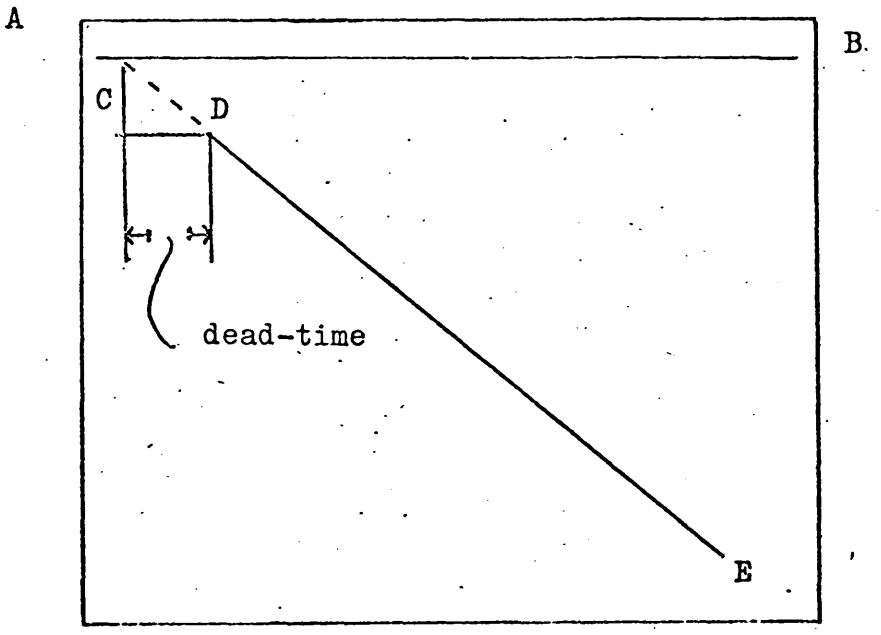
A :- Camera aperture

BC :- Graticule

ED :- Oscilloscope screen

Fig. 1.9

The calculation of the dead-time of a stopped-flow apparatus.



AB represents the transmittance of water

CD represents the transmittance observed at the start of the trace.

DE represents a plot of $\log(A_\infty - A_t)$ versus time.

was derived from a superimposed water line corresponding to the zero absorbance of the newly formed $FeNCS^{2+}$ complex. The dead - time for the stopped flow apparatus (A) using the Unicam S.P. 500 monochromator was found to be 15ms., the second type (A^1) using the Hilger (A^1) was 35ms - and the third type (B) using the SP 800 was experimentally estimated to be 300 $\pm$ 50 ms.

Preparation of Reagents

In all the investigations carried out, the ionic strength of the medium was maintained constant at 1M using mixtures of sodium perchlorate (Fluka puriss p.a.) and perchloric acid (A.R.). The perchlorate ion was used because of its poor co-ordinating properties. In some cases, lithium perchlorate was used as the added electrolyte instead of sodium perchlorate to investigate the effect of the cations on the rate of reaction. Changes in rate of between 10 - 20% have been reported by some workers[76,77] on replacing sodium ions by lithium ions. This effect was not observed in our investigations.

All solutions were made using water prepared from an all glass still. Concentrations of stock solutions of perchloric acid were determined by titration against weighed quantities of sodium tetraborate using methyl red as indicator while those of sodium perchlorate were estimated gravimetrically. 2ml of the latter were pipetted out

accurately into a weighed bottle and dried in an oven at 120°c. From the residual weight the molarity was evaluated.

Lithium perchlorate was prepared by the action of perchloric acid on lithium carbonate.

$$Li_2CO_3 + 2H\,ClO_4 \longrightarrow 2\,Li\,ClO_4 + H_2O + CO_2$$

The salt obtained was recrystallised several times in water and made into solution with distilled water. Standardisation of the solution was carried out by passing a known amount down a cation exchange column in the hydrogen form and the amount of hydrogen ions released was estimated by titration against standard sodium hydroxide. The concentration of the original stock of lithium perchlorate was calculated from the average titre obtained.

Characterisation of the Products

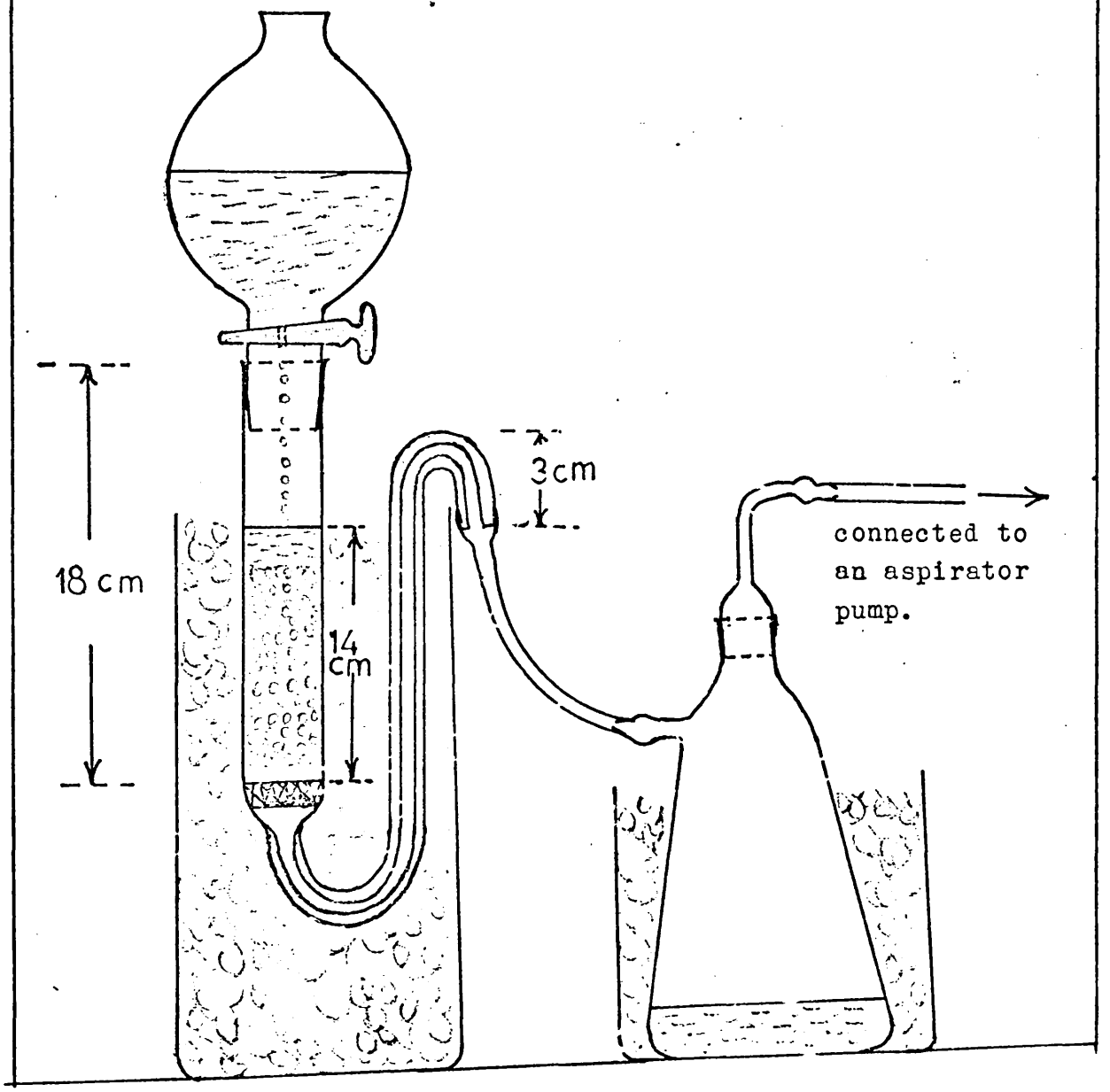
In redox reactions between a metal ion and both metal and non-metallic substrates product analysis does give some indication as to the nature of the transition state preceding the electron transfer. This is particularly significant in the Cr(VI) oxidation reduction reactions[29] where the final product is Cr(III). Since the bulk of the work carried out involved this metal ion, investigations have been made on isolation and characterisation of the various products. Individual products which have been identified will be discussed under appropriate chapters.

Ion - Exchange Technique

Isolation of the various Cr(III) complexes so formed was carried out using a specially constructed ion-exchange column shown in Fig 1.10. The column was 18cm long and 1cm internal diameter, with a 250ml. Separating funnel as a reservoir. A glass Sinter was also incorporated as shown. The column was filled with cation exchange resin (Dowex 50W - X8, 100 - 200 mesh) in the hydrogen form to a level just below the capillary tube (outlet) level. In so doing, the possibility of the column running dry was eliminated. The flow rate was controlled by appropriate adjustment of the reservoir tap and the choice of the Sinter used.

The entire column with the exception of the tip of the exit tube and reservoir was immersed in an ice bath. This was not only to minimise hydrolysis or aquation of the Cr(III) products but also to ensure that each species came down as a discrete band. The possibility of aquation reaction was further minimised by taking the desired species off the column as rapidly as possible. This was achieved by fitting a filter flask to the column outlet and creating a partial vacuum in the flask by means of an aspirator pump. Although the band was found[78] not to be as sharp as when a slow eluting rate was used, efficiency of separation was achieved by first allowing the various species to separate using a slow eluting rate and appropriate solvent mixtures

Fig. 1.10



Specially constructed ion exchange column used for the isolation and characterisation of some chromium (III) complex products.

before applying pressure through the aspirator pump.

Before the column was used, it was first flushed through with 2M $HClO_4$ to remove any cationic species which might be present in the resin and then thoroughly rinsed with distilled water to eliminate the free or excess acid. The reaction mixture was then transferred to the resin through the reservoir. Appropriate solution mixtures were then used in eluting the various species on the column.

In eluting the differently charged thiocyanate complexes of Cr(III) King and Dismukes[79] found different concentrations of $HClO_4$ quite adequate. For example, for the negatively charged, neutral and unipositive complex ions they used 0.15M $HClO_4$. In the case of the di-positive species they used 1.0M $HClO_4$ while for the tripositive $Cr(H_2O)_6^{3+}$, acid concentration not less than 1.5M was used as the eluting solvent. This method has been utilised by a number of workers amongst whom were Moore and Keller[78], Olson and Behnke[80] etc. Although no change in the spectra of these species was observed by Olson and Behnke in the acid concentrations $\sim$ 1.0M, some of the products of the systems investigated showed visible signs of aquation within 3-6 hours of the commencement of the reactions at room temperature. To prevent or at least minimize this, different concentrations of $HClO_4$ and $NaClO_4$ mixtures were used in each case as the eluting solvent with the concentration of the acid kept as low as possible. 0.10M $HClO_4$ was first used for negatively charged neutral or unipositive species. With 0.5M $HClO_4$ as

eluant, slight movement of the dipositive species was observed which rapidly came off the column when 0.1M $HClO_4$ and 1M $NaClO_4$ mixture was used. The tripositive cations always moved very slowly with 0.1M $HClO_4$ and 1.0M $NaClO_4$ but came down more rapidly with 0.1M $HClO_4$ and 2M $NaClO_4$ mixture. Using a fairly high concentration of $NaClO_4$ (~5M), it was possible to isolate any desired species with a concentration as high as 0.01M.

The spectra of such concentrated species were obtained in some cases using SP 800 spectrophotometer. The chromium content of the fractions was determined using bromine oxidation in basic media with spectroscopic estimation of the resultant CrO_4^{2-} at λ = 372nm (ε = 4810 $l\,mol^{-1}\,cm^{-1}$)[81]. Estimation of the amount of sulphur in the solutions was achieved gravimetrically.[82,83] On completion of the Cr^{III} oxidation process above the same solution was boiled with a mixture of nitric acid and perchloric acid for one to two hours. After all the hydrogen bromide gas had been expelled, the solution was allowed to cool to room temperature and the Cr(VI) ions in this fraction were reduced to Cr(III) using ferrous chloride. A solution of $BaCl_2$ was then added. The $BaSO_4$ precipitate was allowed to settle after which it was filtered using an ashless filter paper. The weight of $BaSO_4$ was obtained by difference after igniting and hence the number of moles of sulphur was calculated.

One of the main problems associated with this method

is that low concentrations of sulphur were being determined in each case; this restriction is imposed by the fact that low initial concentrations of Cr(VI) have to be used to prevent parallel reaction between $Cr_2O_7^{2-}$ and the ligand which could result in more complicated products being formed. The method however was tested by using a known, concentration of sulphur in the form of thiourea and a result to ±5% was obtained.

Another factor which might give rise to low values of sulphur content is the loss of gaseous products[84] such as SO_2 and H_2S which might be formed during the course of oxidation of the sulphur. Clearly, alternative means of characterising low sulphur concentration are required.

CHAPTER II

SOME FEATURES OF THE CHEMISTRY OF CHROMIUM VI

The highest oxidation state for chromium as for Titanium and Vanadium corresponds to the loss of all the 3d and 4s electrons. Chromium (VI) is the more strongly oxidising, however. The oxidative properties of the metal ion are of considerable importance in both volumetric analysis and in the oxidation of some organic materials. It is used in the form of potassium dichromate in the former and chromic acid in the latter.

In aqueous solution, Chromium (VI) exists in several oxyanionic forms. Above pH5, the dominant species is the chromate ion CrO_4^{2-}. In acid solution, however, the nature of the species present is not as well defined not only because of the protonation of CrO_4^{2-} to give $HCrO_4^-$ (ref 85) and H_2CrO_4 (ref 86) but also because of the condensation reactions to give dichromate $Cr_2O_7^{2-}$ and possibly larger molecules which may also be protonated. Table 2.1 gives the protonation constants of these chromium (VI) species. In dilute acid solutions, the predominant form of chromium (VI) is $HCrO_4^-$ when $[Cr(VI)]$ is $< \sim 10^{-3}$ M.[85-87]

In recent years, detailed kinetic studies coupled with a wide variety of mechanistic investigations[29,88-90] of the reduction of chromium (VI) by both organic and inorganic substrates have revealed the complex nature of these reactions. This might be expected in a situation where the attainment of a lower stable oxidation state involves the transfer of

TABLE 2.1

Protonation constants of chromium (VI) species at 25°C.

			Refs.
$HCrO_4^-$	$K_{11} = \frac{[HCrO_4^-]}{[H^+][CrO_4^{2-}]}$	$= 1.04 \times 10^6$	(a)
H_2CrO_4	$K_{21} = \frac{[H_2CrO_4]}{[H^+][HCrO_4^-]}$	$= 0.21$	(b)(c)(d)(e)
$HCr_2O_7^-$	$K_{12} = \frac{[HCr_2O_7^-]}{[H^+][Cr_2O_7^{2-}]}$	$= 0.03$	(b)(c)(d)

(a) G. Schwarzenbach and J. Meier, J. Inorg. Nucl. Chem; 8, 302 (1958).

(b) J.Y. Tong and E.L. King, J. Amer. Chem. Soc., 75, 6180 (1953).

(c) G.P. Haight, D.C. Richardson and N.H. Colburn, Inorg. Chem; 3, 1777 (1964).

(d) J.Y. Tong Inorg. Chem. 3, 1804 (1964).

(e) J.Y. Tong and R.L. Johnson, Inorg. Chem. 5, 1902 (1966).

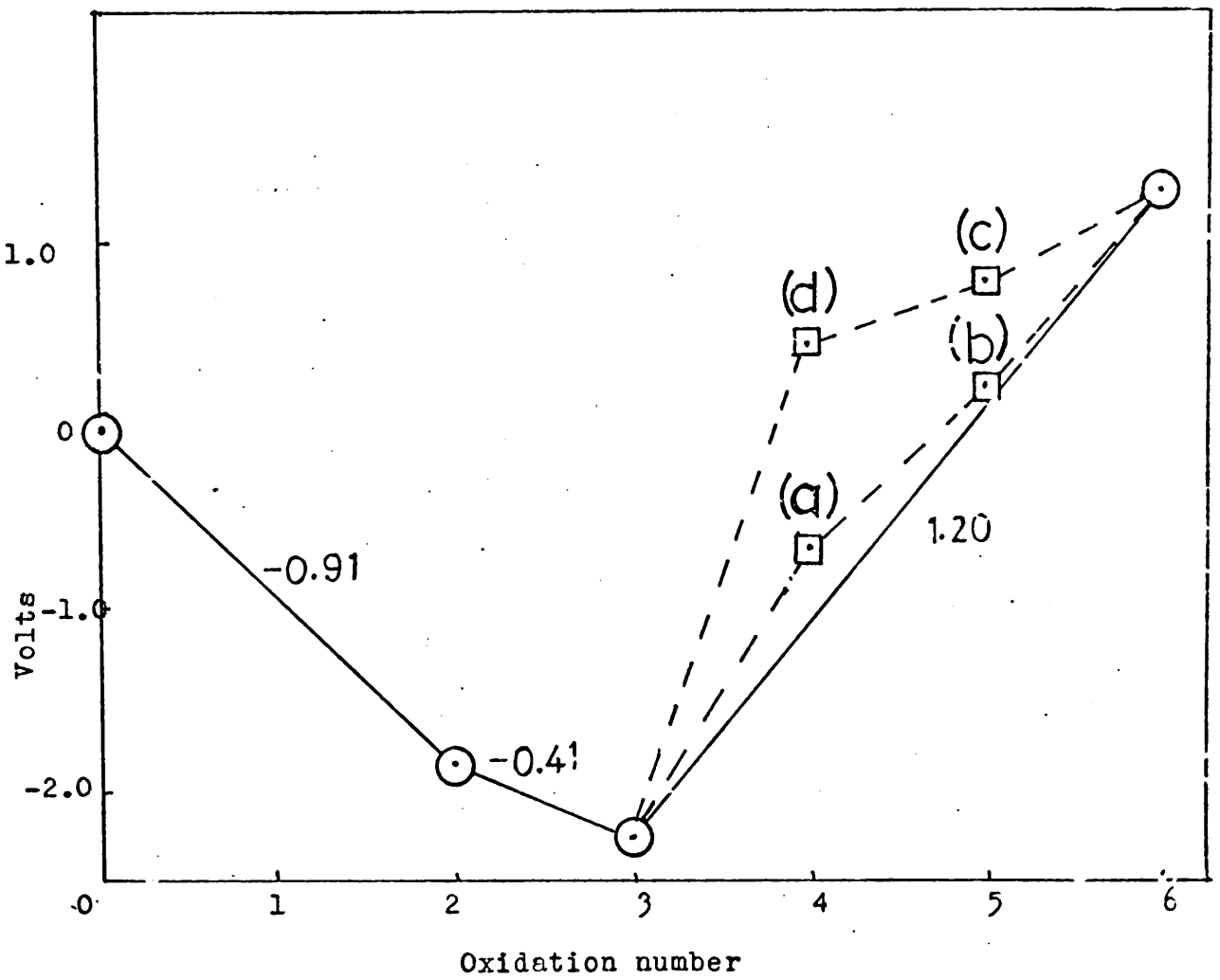
three electrons. Almost all known redox reactions involve the transfer of no more than a pair of electrons in one step. The reduction of chromium (VI) to the stable +3 state usually proceeds in a similar manner, with chromium (V) and chromium (IV) being formed as intermediates. A small number of cases however, have been reported where chromium (VI) appears to accept three electrons simultaneously.[91,92] The ability of $HCrO_4^-$ to form esters with electron - pair donors particularly those with hydroxyl groups, is already well established[29] and a list of some complexes of this type which has been characterised to date is given in Table 2.2 The co-ordination of reductants to the chromium centre in a step preceding the redox process has been observed in a number of reactions of this oxidant.[29]

Information on the elementary steps leading to the transition state for the redox processes can be obtained from characterisation of the intermediates and establishment by means of the rate law of the composition of the activated complexes. Also from identification of the inert chromium (III) complexes which are the final products, it is possible to make deductions on the elementary steps which might take place after the transition state.

<u>The Nature and the Role of Chromium (V) and Chromium (IV) in Chromate (VI) oxidations</u>

Although the positions of chromium (IV) and chromium (V) in the Frost diagram shown in Fig 2.1 are estimated limits,

Fig 2.1



Frost diagram for chromium. The points for Cr(IV) and Cr(V) are estimated limits; point (a) from the capture of Cr(IV) by Ce(III), Point (c) from the reversible reduction of Cr(VI) to Cr(V) by Fe(II) and the slow oxidation of iodide by Cr(VI), and points (b) and (d) from the capture of Cr(IV) by Cr(VI).

they are nevertheless representative of the general trend observed in the mechanistic investigations of the chromium (VI) oxidations. For example, the diagram predicts that chromium (IV) will disproportionate, react with chromium (VI) or be reduced easily to chromium (III) all of which are features of various mechanisms encountered.

A. Chromium (V)

A limited number of salts of chromium (V) have been both isolated and identified. Salts of CrO_4^{3-} have been isolated from strongly basic solutions and contain tetrahedral chromate (V) ion.[93] Octahedral salts of chromium (V) ($CrOCl_5^{2-}$), have also been prepared from concentrated HCl solutions and Espenson[90] has provided kinetic evidence that H_3CrO_4 is the chromium (V) species formed in the one equivalent reduction of $HCrO_4^-$ in acidic solutions.

Chromium (V) which has a d^1 electronic configuration can be generated in a number of ways in solution.

(a) By one equivalent reduction of chromium (VI) either by a substrate or by active intermediates, such as chromium (IV) or radicals derived from the substrate. Radicals may also be produced in one step three - equivalent reductions of chromium (VI) which may then reduce a second chromium (VI) to chromium (V).

(b) By disproportionation of chromium (IV) formed from the reduction of chromium (VI) by two - equivalent

substrates.

The formation of chromium (V) has been detected both by E.P.R. spectrometry[95-97] and visible spectrophotometry.[95-98] The reactivity patterns of chromium (V) have been found to be very similar to those of chromium (VI)[91b,97,98] but the former is thought to be slightly less reactive than the latter. This is certainly the case in the chromium (VI) oxidation of isopropanol in 97% acetic acid (ref 99) and also in the reduction of chromium (VI) by oxalic acid.[97]

Examination of the chromium (III) products of some oxidation reactions involving chromium (VI) reveal ligand incorporation of oxidised products.[100,101] These are reactions presumed to involve a two-equivalent reduction of chromium (V). A corollary from this and other observations is that ligand incorporation of oxidised products occurs during or after the reduction of chromium (V), while ligand incorporation of the original substrate takes place at chromium (IV) because of its presumed lability.

B. Chromium (IV)

Only a few complexes of chromium (IV) have been isolated;[102,103] this scarcity has been attributed to the high oxidative power of the ion.[103] All information on chromium (IV) in aqueous systems have been inferred from mechanistic studies. For example, it is widely believed to be octahedral since the reduction of chromium (V) to chromium (IV) (or vice versa) is in many cases the slow step

in the one - equivalent reduction of chromium (VI) to chromium (III). It is also very labile to substitution since inert chromium (III) complexes of non - reducing ligands and unoxidised reagent are observed in reaction products.[104,105] The oxidising power of this ion is greater that that of either the +6 or +5 chromium species.

Chromium (IV) may be formed by two equivalent reduction of chromium (VI) or by one equivalent reduction of chromium (V) by a substrate or radical. Direct observations of this intermediate have not yet been reported but indirect experimental evidence shows that there are four possible ways by which the participation of this ion as an intermediate in the overall reduction of chromium (VI) to the 3+ state may be postulated.

(a) one electron oxidation by chromium (IV)

(b) oxidation of chromium (IV) by chromium (VI)

(c) disproportionation of chromium (IV)

(d) evidence from chromium (III) products.

(a) and (b) can be treated simultaneously if induced oxidation of manganese (II) is considered. The direct oxidation of Mn^{2+} by $HCrO_4^-$ is thermodynamically unfavourable. However in the presence of other two equivalent reducing agents Mn(II) can be rapidly oxidised to Mn^{3+} or possibly MnO_2. This reaction which has been used as an effective trap for chromium (IV) involves one electron transfer (1)

$$Cr\ (IV) + Mn^{2+} \longrightarrow Cr\ (III) + Mn^{3+} \qquad (1)$$

$$2\ Mn^{3+} \longrightarrow MnO_2 + Mn^{2+} \qquad (2)$$

That the reaction could proceed to completion within a relatively short time is a pointer to the participation of chromium (IV). If the overall rate of the redox reaction between chromium (VI) and the substrate is decreased by half on addition of Mn(II), then the mechanism postulated by Westheimer[88] where a second chromium (VI) reduces the intermediate Cr (IV) formed from the first step is most likely to be operating. This effect is observed in the reduction of chromium (VI) by isopropanol in aqueous perchloric acid[88] and by Arsenic (III),[88] and hydrazine[105] to mention only a few examples. Indirect evidence for the existence and subsequent disproportionation of chromium (IV) to chromium (V) and chromium (III) has been provided in the reduction of chromium (VI) by excess hydrazine.[105]

Inferences can also be drawn regarding the participation of chromium (IV) in some chromium (VI) oxidations from the presence of unoxidized substrate insome chromium (III) products.

Mechanism of Tetrahedral Chromate (VI) Substitution

It has been known for some years that it is possible to replace the oxide ions in CrO_4^{2-} by other electron pair donors when acid is present. Substitution reactions such as

$$X^{n-} + HCrO_4^- + H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CrO_3X^{n-} + H_2O \qquad (3)$$

$$HX^{n-} + HCrO_4^- + H^+ \underset{k_b^{H^+}}{\overset{k_f^{H^+}}{\rightleftharpoons}} CrO_3X^{(n+1)+} + H_2O + H^+ \qquad (4)$$

occur readily and lead to more or less stable species in solution.

A number of oxidations appear to proceed by mechanisms wherein the reducing agent becomes substituted in the co-ordination shell of the chromium atom. The conversion of isopropyl alcohol to acetone by chromic acid was postulated by Weistheimer[88] to involve the formation of chromate esters which undergo internal oxidation - reduction. Spectrophotometric measurements have since confirmed the involvement of such esters in the oxidation of isopropyl alcohol in aqueous solution.[95,98] Ester formation has also been observed for a number of reactions involving phosphorus (III) and phosphorus (I) compounds with chromium (VI). Formation of these complex species in the latter case infact appears to be a prerequisite for electron transfer. A clear demonstration of this is the oxidation of hypophosphorous acid by chromium (VI).[106] At pH~0, H_3PO_2 forms an ester and is oxidised by $HCrO_4^-$ whereas at pH 4-5, the predominant species $H_2PO_2^-$, lacking an ^-OH group does not form an ester and is consequently not oxidised.

Changes in the electronic absorption spectra of $HCrO_4^-$ in the presence of subtrates such as HSO_4^- (ref 107), $H_2PO_4^-$ (ref 108), $HPHO_3^-$ (ref 109), $HS_2O_3^-$ (ref 110) and NCS^- (ref 104) are interpreted as indicating formation of the 1:1 esters and the equilibrium constants for these esters are given in Table 2.2.

TABLE 2.2

Chromate(VI) Ester Formation Constants at 25.0°C.

Complex	I/M	K/M^{-1}	ref.
$HOCrO_3^- + HOCrO_3^- \rightleftharpoons [O_3CrOCrO_3]^{2-} + H_2O$	1.0	98	a
$HOCrO_3^- + HOSO_2^- \rightleftharpoons [O_3CrOSO_2]^{2-} + H_2O$	0.5	36	b
$HOCrO_3^- + HOSO_3^- \rightleftharpoons [O_3CrOSO_3]^{2-} + H_2O$	3.0	4.1	c
$HOCrO_3^- + HSSO_3^- \rightleftharpoons [O_3CrSSO_3]^{2-} + H_2O$	0.17	1.24×10^4	d
	0.11	1.1×10^4	e
$HOCrO_3^- + HOP(=O)H_2 \rightleftharpoons [O_3CrOP(=O)H_2]^- + H_2O$		11	f
$HOCrO_3^- + HOP(=O)(OH)H \rightleftharpoons [O_3CrOP(=O)(OH)H]^- + H_2O$		16	f
$HOCrO_3^- + HOP(O)_2H^- \rightleftharpoons [O_3CrOP(O)_2H]^{2-} + H_2O$		7	f
	3.0	8	g
$HOCrO_3^- + HOP(=O)(OH)_2 \rightleftharpoons [O_3CrOP(=O)(OH)_2]^- + H_2O$	0.25	9.4	h
$HOCrO_3^- + HOP(O)_2OH^- \rightleftharpoons [O_3CrOP(O_2)OH]^{2-} + H_2O$	0.25	2.9	h
	3.0	6	i
$HOCrO_3^- + HOAs(OH)O^- \rightleftharpoons [O_3CrOAs(OH)O]^{2-} + H_2O$		22	j
$HOCrO_3^- + HOC(=O)CH_3 \rightleftharpoons [O_3CrOC(=O)CH_3]^- + H_2O$	1.0	1.5	k
$HOCrO_3^- + HONH_2 \rightleftharpoons [O_3CrONH_2]^- + H_2O$	1.0	1.2×10^3	k
$HOCrO_3^- + HNHNH_3^+ \rightleftharpoons [O_3CrNHNH_3] + H_2O$	1.0	3.2	l
$H^+ + HOCrO_3^- + Cl^- \rightleftharpoons [O_3CrCl]^- + H_2O$	1.0	17*	c
	1.0	11*	m
$H^+ + HOCrO_3^- + SCN^- \rightleftharpoons [O_3CrSCN]^- + H_2O$	0.3	220*	n

* Units are M^{-2}

(a) J.Y. Tong and E.L. King, J. Amer. Chem. Soc., 1953, 75, 6180.

(b) G.P. Haight, E. Perchonock, F. Emmenegger, and G. Gordon, J. Amer. Chem. Soc., 1965, 87, 3835.

(c) G.P. Haight, D.C. Richardson and N.H. Coburn, Inorg. Chem., 1974, 3, 1777.

(d) I. Balden and G. Niac, Inorg. Chem., 1968, 7, 1232.

(e) K.M. Muirhead, G.P. Haight, and J.K, Beattie, J. Amer. Chem. Soc., 1972, 94, 3006.

(f) G.P. Haight, M. Rose, and J. Preer, J. Amer. Chem. Soc., 1968, 90, 4812.

(g) S.A. Frennesson, J.K. Beattie, and G.P. Haight, Acta. Chem. Scand., 1969, 23, 3277.

(h) F.Holloway, J. Amer. Chem. Soc., 1952 74, 224.

(i) S.A. Frennesson, J.K. Beattie and G.P. Haight, J. Amer. Chem. Soc., 1968, 90, 6018.

(j) J.G. Mason and A.D. Kolowak, Inorg. Chem., 1964, 3, 1248.

(k) R.A. Scott, G.P. Haight, and J.N. Cooper, J. Amer. Chem. Soc., 1974, 96, 4136.

(l) G.P. Haight, T.J. Huang, and H. Platt, J. Amer. Chem. Soc., 1974, 96, 3137.

(m) J.Y. Tong and R.L. Johnson, Inorg. Chem., 1966, 5, 1902.

(n) C.T. Lin and J.K, Beattie, J. Amer. Chem. Soc., 1972, 94, 3011.

A controversy has arisen over the nature of the general mechanism of the acid-catalysed substitution of ^{-}OH in the hydrogen chromate anion.[104,111] All rate constants so far determined for such reactions have values in the range (1-7 x 10^5 l^2 mol^{-2} S^{-1} (Table 2.3).

In an attempt to correlate the insensitivity of the formation rate constants to the nature of the incoming ligand for these reactions, Lin and Beattie[104] postulated that this phenomenon was a result of the rate-determining step being diffusion-controlled protonation of hydroxyl ion. The mechanism suggested involves three stages:

$$HX + HCrO_4^- \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} X(H)\cdots CrO_3(OH) \qquad K_o = \frac{k_o}{k_{-o}} \qquad (5)$$

$$H^+ + X(H)\cdots CrO_3^-(OH) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X - CrO_3^-(OH_2) + H^+ \qquad (6)$$

$$X - CrO_3^-(OH_2) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X - CrO_3^- + H_2O \qquad (7)$$

The first stage (5), is the diffusion-controlled formation of a weak complex and the second, (6) involves diffusion-controlled protonation of ^{-}OH co-ordinated to the chromium centre, with subsequent loss of a proton from the substrate resulting in the formation of a fully 5 - co-ordinate intermediate. Since the reaction is acid dependent it was reasoned that the rate determining step would occur at either (6) or (7) but in view of the fact that the acid catalysed rate constants for the anation reaction, $k_f^{H^+}$ are independent of the acid strength of the substrate,

TABLE 2.3

Chromate(VI) Ester Formation Rate Constants at 25.0°C as Measured in Other Laboratories

($k_f^{H^+}$ is the specific rate for the hydrogen-ion-dependent pathway.

k_f is the specific rate for the hydrogen-ion-independent pathway.)

Substrate	I/M	$k_f^{H^+}/l^2mol^{-2}s^{-1}$	$k_f/lmol^{-1}s^{-1}$	ref.
$HCrO_4^-$	1.0	6.2×10^5	-	(a)
	0.1	-	2	(b)
$H_2PO_4^-$	3.0	1.2×10^5	-	(c)
$H_2PO_3^-$	3.0	5.0×10^5	-	(d)
$HS_2O_3^-$	0.11	-	2×10^4	(e)
$S_2O_3^-$	0.11	(3.7×10^5)*	-	(e)
SCN^-	0.3	5.4×10^5	-	(f)
$(NH_3)_5CoOH^{2+}$	0.25	4.0×10^5	-	(g,h)
$(NH_3)_4Co(OH_2)OH^{2+}$	0.25	4.0×10^5	-	(g.h)

* Calculated on the basis of the alternative interpretation of the rate data by A. Haim, Inorg. Chem., 1972, 12, 3147.

(a) J.R. Pladziewicz and J.H. Espenson, Inorg. Chem., 1971, 10, 634.

(b) J.H. Swinehart and G.W. Castellan, Inorg. Chem., 1964, 3, 278.

(c) S.A. Frennesson, J.K. Beattie, and G.P. Haight, J. Amer. Chem. Soc., 1968, 90, 6018.

(d) S.A. Frennesson, J.K. Beattie, and G.P. Haight, Acta Chem. Scand., 1969, 23, 3277.

(e) K.A. Muirhead, G.P. Haight, and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3006.

(f) C.T. Lin and J.K. Beattie, J. Amer. Chem. Soc., 1972, 94, 3011.

(g) M. Woods and J.C. Sullivan, Inorg. Chem., 1973, 12, 1459.

(h) G.P. Haight, Inorg. Chem., 1973, 12, 1461.

it was concluded that proton transfer took place after the transition state and that the rate determining step was (b).

On the basis of this mechanism

$$k_f^{H+} = K_o k_1 \qquad (8)$$

A value of between 10^{-4} and 10^{-5} mol^{-1} was calculated [112] for K_o to justify the proposed weak bonding between $HCrO_4^-$ and the substrate in the transition state .

Haim[111] on the other hand, showed that for k_{-o} to have a physically possible value, k_o must be less than $\sim 5 \times 10^4$ $l\ mol^{-1}\ s^{-1}$. He also expressed doubt that k_o would in reality be as invariant as would be required by this scheme and concluded that the more likely mechanism is one involving protonation of $HCrO_4^-$ as the first step with loss of water being rate determining . Similar investigations carried out with sulphur - containing reducing agents were performed to shed some further light on the mode of these anation reactions.

Reactions of chromium (VI) with one-equivalent reductants

Reduction of chromium (VI) by one - equivalent reducing agents and principally metal - ion reductants, has recently been reviewed by Espension.[90] The reduction is thought to proceed by a sequence of one electron steps with (10) as the rate - determining step.

$$Cr\ (VI) + M^{n+} \rightleftharpoons Cr\ (V) + M^{(n+1)} \qquad (9)$$

$$Cr\ (V) + M^{n+} \rightleftharpoons Cr\ (IV) + M^{(n+1)+} \qquad (10)$$

$$Cr\ (IV) + M^{n+} \rightleftharpoons Cr\ (III) + M^{(n+1)+} \qquad (11)$$

This mechanism was first proposed by King[113] who also postulated that (10) is the slow step consistent with the difficult rearrangement required to expand the chromium co-ordination from four to six. However, the possibility of (9) being the rate - determining step cannot be ruled out. One of the steps could also involve an inner sphere activated complex, since oxidised products are found co-ordinated with chromium (III).

Evidence for this reaction scheme comes from the form of the rate laws observed, the induction ratios obtained by the induced oxidation of iodide ion, and identification of the products in the oxidation of V^{2+} (ref 29) and V^{3+} (ref 114).

Reactions of Chromium (VI) with two-equivalent reductants

Many reagents are capable of effecting a two equivalent reduction of chromium (VI) to chromium (IV as the first step in the overall reduction to chromium (III). The mechanisms of these redox reactions are best described by considering the steps leading to the formation of the chromium (IV) and the subsequent fate of this intermediate. The latter aspect has been discussed under the role of chromium (IV) in chromium(IV) oxidation reactions and need not be considered further. The formation of chromium (IV) can be discussed in terms of both the nature of the activated complex and the two - equivalent step involved.

Chromate ester species analogous to that formed in the chromium (VI) oxidation of isopropyl alcohol[88] appear to be important intermediates in the redox process. Evidence for their participation is obtained both from the rate laws and by direct observation using stopped - flow techniques. Although their detection does not necessarily imply that they are required for the redox reaction, several cases are known in which the prevention of complex formation inhibits the reduction of chromium (VI).[88,106,115]

The two-equivalent reduction of chromium(VI) to chromium (IV) can occur by a number of processes:

(a) direct two electron transfer

(b) hydride abstraction

(c) inner sphere two-electron transfer and

(d) substrate assisted electron transfer.

(a) is considered unlikely because of the large Franck-Condon re-organisation energies required. Mechanism involving (b) is found in both phosphorus (I) and phosphorus (III) reduction of chromium (VI) where the removal of hydrogen as a proton is a prerequisite for the transfer of a pair of electrons from phosphorus to chromium through an oxygen-bridged intermediate.[106, 115] Case (c) involves the formation of a chromate ester followed by the net transfer of two elctrons. This process is illustrated by the relative reactivities of various phosphorus (III) compounds already mentioned. The last process to be considered (d) is the substrate

assisted electron transfer. The reduction is effected by the attack of the substrate on co-ordinated substrate to give direct formation of a dimer of the radical which could form by one - equivalent oxidation. An example of this process is found in the chromium (VI) oxidation of thiosulphate[116]

$$O_3Cr\ SSO_3^{2-} + S_2O_3^{2-} \longrightarrow Cr\ (IV) + S_4O_6^{2-} \qquad (12)$$

Investigations carried out on the oxidation of a number of sulphur - containing organic ligands by chromium (VI) reveal that the latter process (d) is most likely to be operating and these will be discussed in the subsequent chapters.

C H A P T E R III

OXIDATION OF THIOUREA AND ITS N - SUBSTITUTED DERIVATIVES BY CHROMIUM (VI)

Introduction

Reactions of chromium (VI) with sulphur - containing ligands have been the subject of several recent studies.[92,104,110,112,117] In some instances the formation of Cr - S bonded intermediates has been postulated, the species being characterised by a red shift of charge - transfer band in the near U.V. region. Formation constants for such transient sulphur - bonded esters have also been found to be significantly larger than those of the corresponding oxygen - bonded species.[29] This is interpreted as indirect evidence for a metal sulphur linkage. For example, the anions, hydrogen sulphite,[101] HSO_3^- and hydrogen sulphate,[107] HSO_4^- both form 1:1 chromate esters with formation constants of 36 and 4 1 mol^{-1} respectively. Reference to Table 2.2 shows that these values are of the same order of magnitude found for esters in which the substrate is linked to the chromium centre by oxygen whereas, the ion $HS_2O_3^-$, which is considered to be sulphur bonded to chromium, forms a complex which has a formation constant of $\sim 10^4$ 1 mol^{-1}.[110,116] Also in the oxidation reactions of thiocyanate[117] and thiosulphate,[110,116] paths involving second order terms in the ligand have been observed[110,116] consistent with an increase of the co-ordination number of the chromium (VI) complex ion in the transition state.

The above findings make the study of the kinetics and mechanism of the chromium (VI) oxidation of thiourea,

NN^1 - ethylenethiourea, N - methyl and NN^1 - dimethyl thiourea of interest for several reasons.

(a) complex formation has been observed in each case and the data obtained in these studies may be readily compared with those of other ligands[117] where the possibility may arise of either N- or S- co-ordination to the metal centre. If the former is the case then the greatly increased steric hindrance in the reaction of the N-substituted derivatives should be reflected in the thermodynamic parameters for complex formation.

(b) It is also of interest to compare the rate laws in these studies with that for the reaction of the same oxidant with other sulphur - containing ligands.

(c) The rate of oxidation of several thiourea derivatives by metal ion oxidants such as Cobalt (III)[118,119] and Manganese (III)[120] appears to be controlled by the rate of substitution of the reductant into the inner - co-ordination sphere of the metal ion. Although complex formation was not detected in either case, it is of interest to investigate the analogous reactions with $HCrO_4^-$ which also exhibits substitution control in some of its redox reactions.[29]

Experimental

Potassium dichromate (Analar), sodium perchlorate (Fluka, puriss p.a.) and perchloric acid were used without further purification. Thiourea (B.D.H.) and NN^1-ethylenethiourea (Aldrich) were recrystallised twice from ethanol - water (50/50 V/V) and NN^1- dimethylthiourea (Aldrich) from dioxan. N - methyl thiourea was used without further purification and analyses of the compounds gave results consistent with at least 99.9% purity.

(a) Kinetics

Solution in large excess of the ligand $[(2.5 - 40) \times 10^{-3}$ M] were mixed with $(2 - 4) \times 10^{-4}$ M $[Cr^{VI}]$ where $HCrO_4^-$ is established to be the predominant species. Kinetic measurements were made using a stopped - flow apparatus described in chapter I with a dead time of the order of 15 milliseconds. A Unicam S.P. 500 monochromator was used as the monochromatic light source. Solutions were allowed to thermostat for at least 30 mins. prior to any readings being taken. Voltage readings at various times from photographs of oscilloscope traces were referred to a known voltage and converted to absolute optical densities using a Nova 1200 computer by the method given in chapter I.

First - order kinetic plots were linear to greater than 85% completion of the reaction and duplicate measurements gave results in agreement to ± 2%. Comparison of initial optical densities with those for solutions of chromium (VI)

of identical concentration showed that a complex was formed within the time of mixing of the reagents. The spectra of the intermediates were derived from the variation of optical densities at t = 0 and those for thiourea and ethylenethiourea are shown in figure 3.1. These spectra have been found to be similar to those of N-methyl-and NN^1-dimethyl-thiourea.

(b) Stoicheiometry

The stoicheiometries of the reactions of all the ligands with chromium (VI) were determined using spectrophotometric titrations. Spectra of solutions containing various concentrations of chromium (VI) in the range (1-40) x 10^{-3}M and a constant ligand concentration (3.2 x 10^{-2}M) were measured after reaction had occurred, the residual chromium (VI) being monitored at wavelengths where there was little or no absorbance from the chromium (III) - complex products.. Similar results were obtained when the reaction products were removed using a cation - exchange column and the unreacted (negatively charged) Chromium (VI) was determined as above. Fig 3.2 and 3.3 show typical titration curves obtained both in the presence and absence of complex products.

Results obtained in all the reactions indicate that 3.0 $\pm$ 0.2 moles of the substrate were consumed per mole of oxidant.

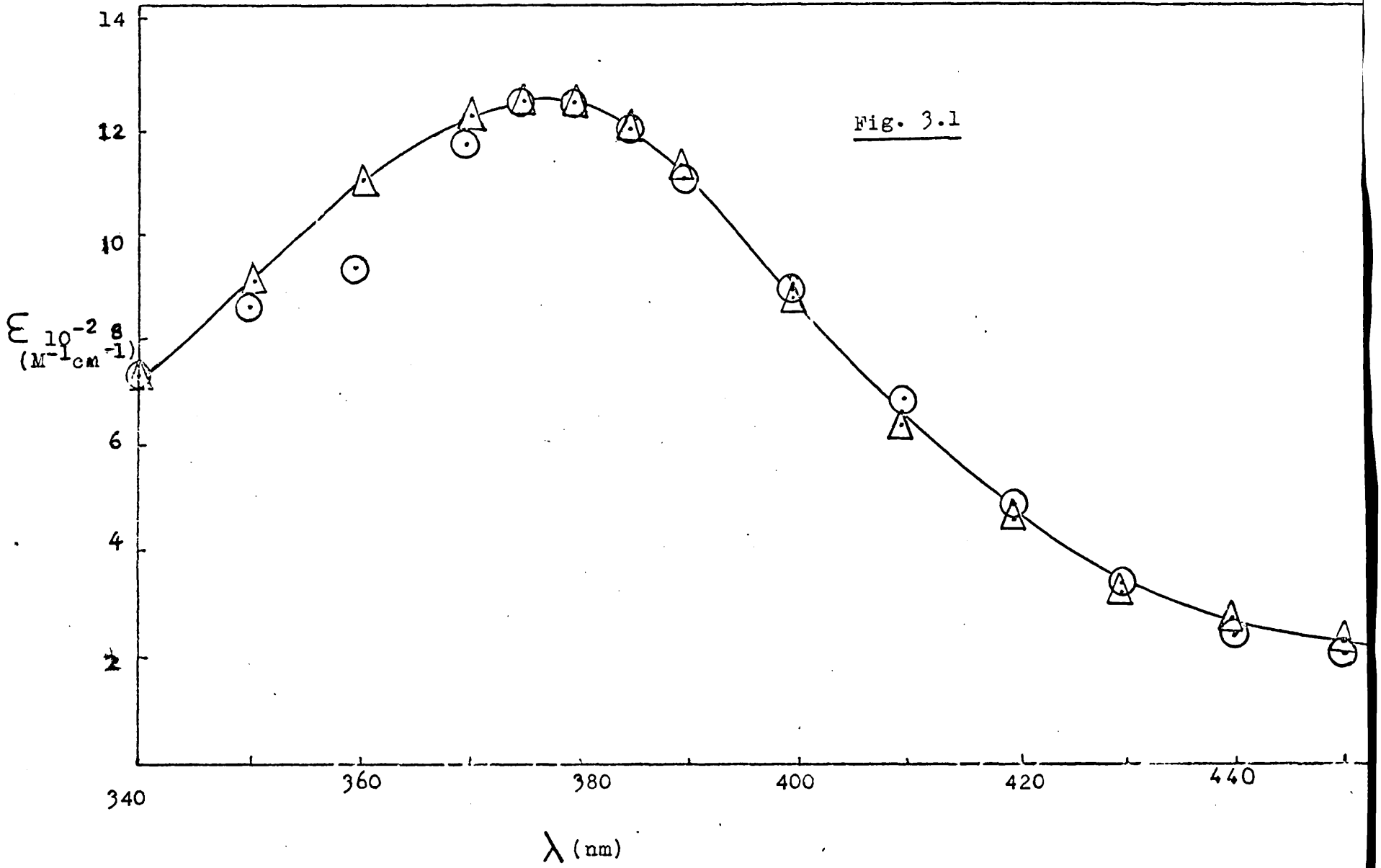
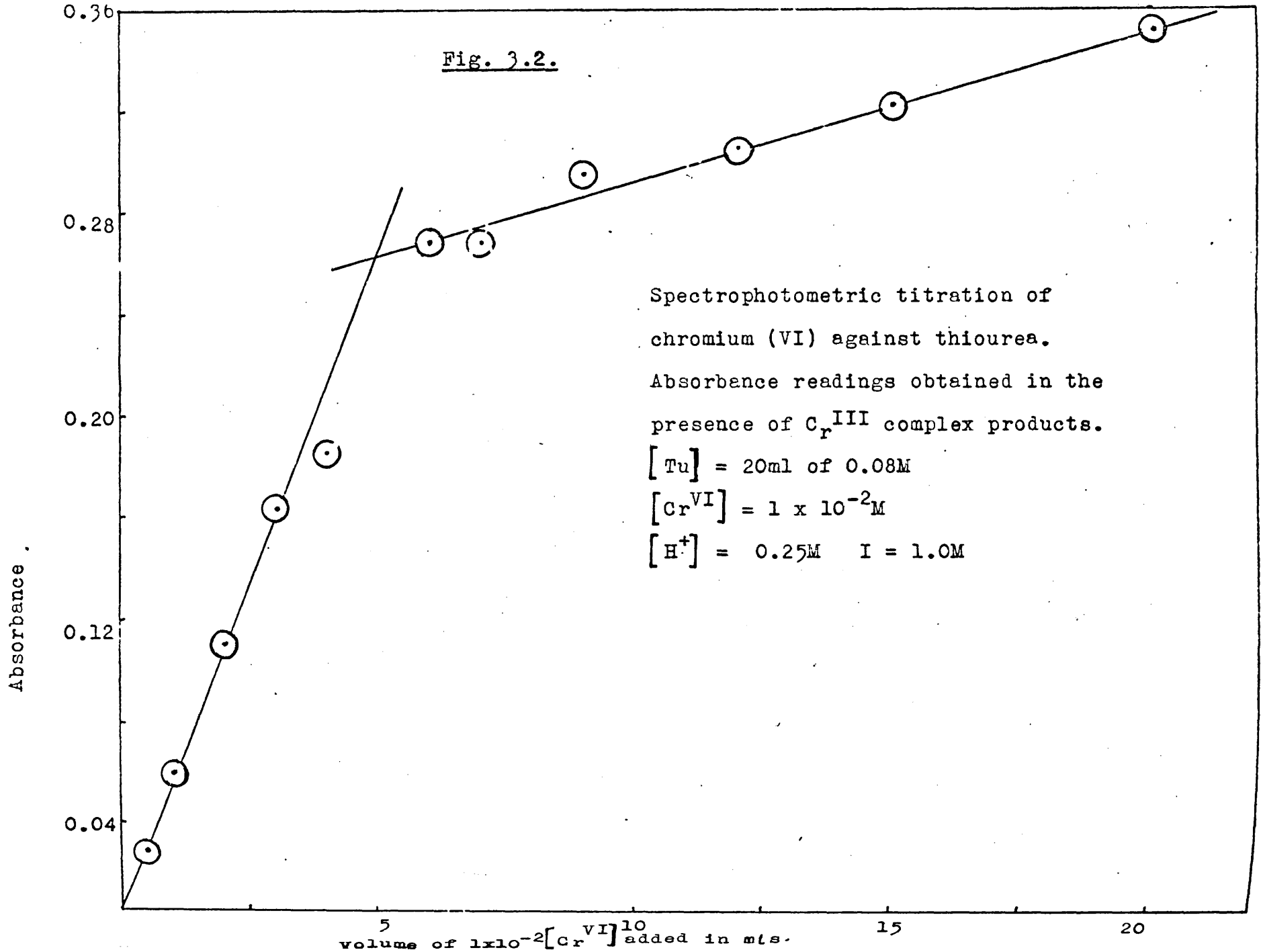


Fig. 3.1

Spectra of intermediate complexes: (⊙), thiourea; (△), NN^1-ethylenethiourea.

Fig. 3.2.

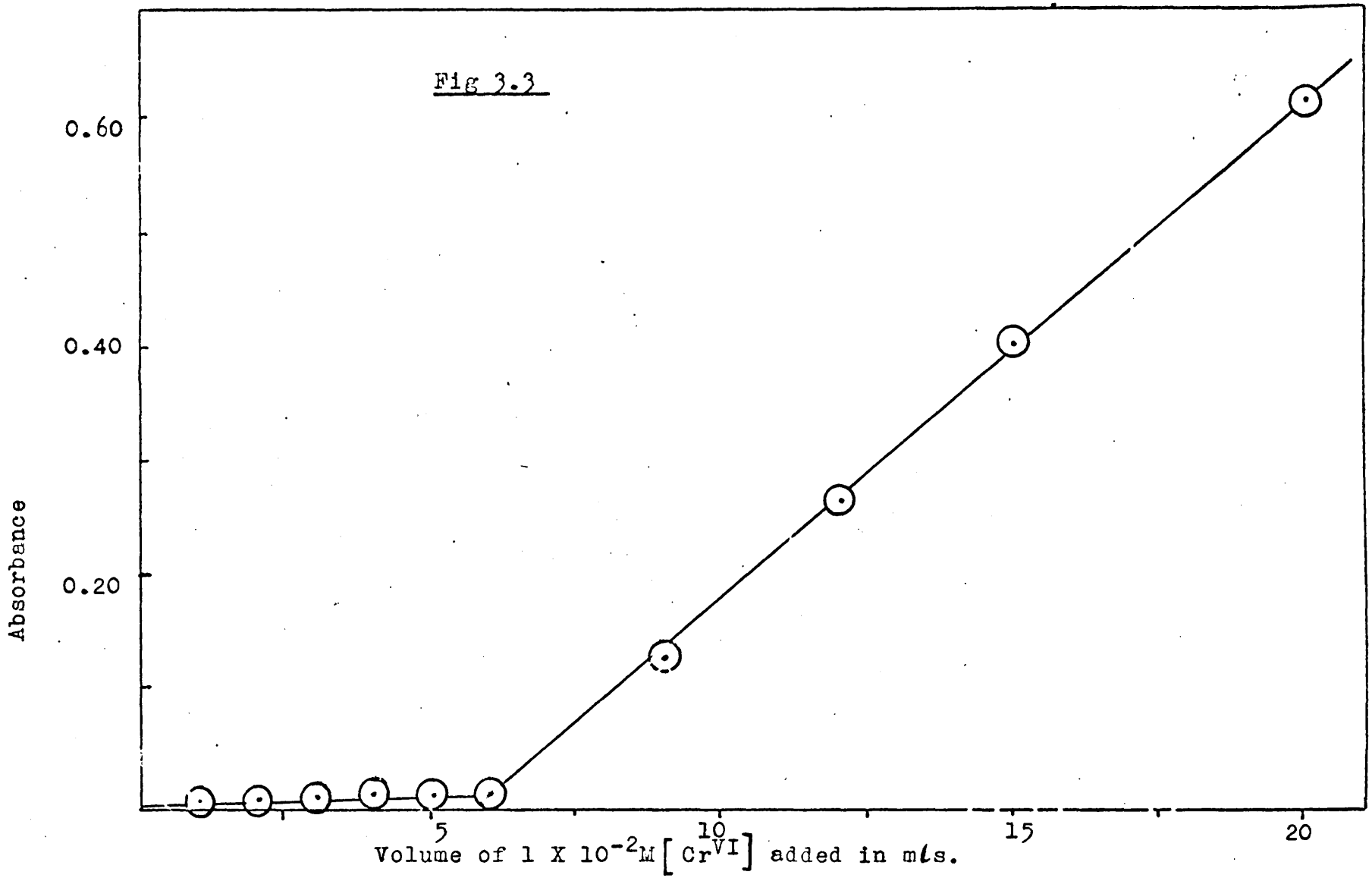


Spectrophotometric titration of chromium (VI) against thiourea. Absorbance readings obtained in the presence of C_r^{III} complex products.

$[Tu]$ = 20ml of 0.08M

$[Cr^{VI}] = 1 \times 10^{-2}$M

$[H^+]$ = 0.25M I = 1.0M



Spectrophotometric titration of chromium (VI) against NN-ethylenethiourea. Absorbance reading obtained at λ = 500nm in the absence of Cr^{III} complex products.
$[Cr^{VI}]$ = 1 X 10^{-2}M; [Ethylenethiourea] = 20ml of 0.08M $[H^+]$ = 0.25M I = 1.0M

(c) Products

Detailed characterisation of the reaction products were carried out in two cases i.e. in the reaction of chromium (VI) with thiourea and ethylenethiourea since preliminary investigations of the products from the reactions involving the other two ligands (methyl-thiourea and dimethyl-thiourea) indicate a trend similar to ethylenethiourea.

In the case of thiourea; a stoicheiometric excess (Ca. 30m mol) of sodium dichromate dissolved in water ($15cm^3$) was added slowly to a cooled acidic (Ca.0.5M) solution ($35\ cm^3$) containing thiourea (50 m mol). The solution rapidly turned green and four volumes of ethanol were added followed by conc. HCl ($50\ cm^3$). On cooling crystals of CC^{l} - dithiobis (formamidinium) hydrochloride were obtained identical to those prepared by hydrogen peroxide oxidation,[121] the S-S bond being confirmed by Raman spectroscopy. The overall half-reaction of thiourea may thus be represented as (1)

$$2\ (NH_2)_2\ CS \rightleftharpoons \left[\begin{matrix} NH_2 \\ \diagdown \\ C \\ \diagup \\ NH_2 \end{matrix}\right]^{+} - S - S - \left[\begin{matrix} NH_2 \\ \diagup \\ C \\ \diagdown \\ NH_2 \end{matrix}\right]^{+} + 2e$$

Further confirmation of this disulphide as a product was given by the ready decomposition to sulphur in acid media.

In the reactions of ethylenethiourea, although the characteristic green colouration of Cr^{III} complexes was given under conditions identical to those above, no

protonated disulphide was precipitated. After such a reaction carried out at $[H^+]$ = 0.25M, however, addition of base increasing the pH to Ca 8 (just prior to any precipitation being evident), followed by diethylether extraction and concentration of the ether solution on a rotary evaporator, yielded a white solid. Elemental analysis was consistent with bis (dihydroimidazol - 2 - ylio) - disulphide and the peak at 502 cm^{-1} in the Raman spectrum confirmed the disulphide linkage.[122] For comparison, the corresponding spectrum of L - cystine was run where a peak at 498 cm^{-1} was observed.

The metal - ion reaction products in the presence of excess of the reductants were hexa - aquochromium (III) and chromium (III) - thiourea complexes together with a small amount of a highly charged ion. Solutions containing 4 x 10^{-3}M Cr (VI), 5 x 10^{-2}M ligand and 0.25M $HClO_4$ were used for this investigation in each case. In the case of thiourea, two cationic species were identified and isolated using a Dowex 50W x 8 (100 - 200 mesh) ion - exchange column described in chapter I. Comparative elution rates with Cobalt (III) - ammine complexes of known charge confirmed these both to be +3 overall charge. Separation was effected using sodium perchlorate - perchloric acid solution as eluant and the spectrum of the non - sulphur - containing fraction was identical with that of $[Cr(H_2O)_6]^{3+}$. In order to determine the total number of moles of reductant reacting with the chromium (VI),

experiments were carried out under exactly the same conditions as those described in which thiourea was in excess. Immediately after reaction an aliquot portion of solution (100ml) was transferred to a Dowex 50W x 8 ion - exchange column described in chapter I.

In previous studies on thiourea and its derivatives, it has been considered[118-120] that one of the nitrogen atoms is protonated in accord with the data of Walter[123] and his co-workers. These data infact relate to dioxan-water mixtures and may not be extrapolated to acidic aqueous media.[124,125] Under such conditions, the pka values of the conjugate acids of thiourea and its derivatives fall in the range - 1.0 to - 1.9 (ref 126,127) so that no protonation would be expected even in the most acidic media studied here. The uncharged unreacted thiourea in the sample transferred to the ion-exchange column was therefore eluted without retention and was monitored using a silver - ion titration in basic media,[128] in which a known volume of silver (I) is added to the thiourea solution. After removal of the silver sulphide formed the excess of silver ion was titrated with ammonium thiocyanate using iron (III) alum as indicator.

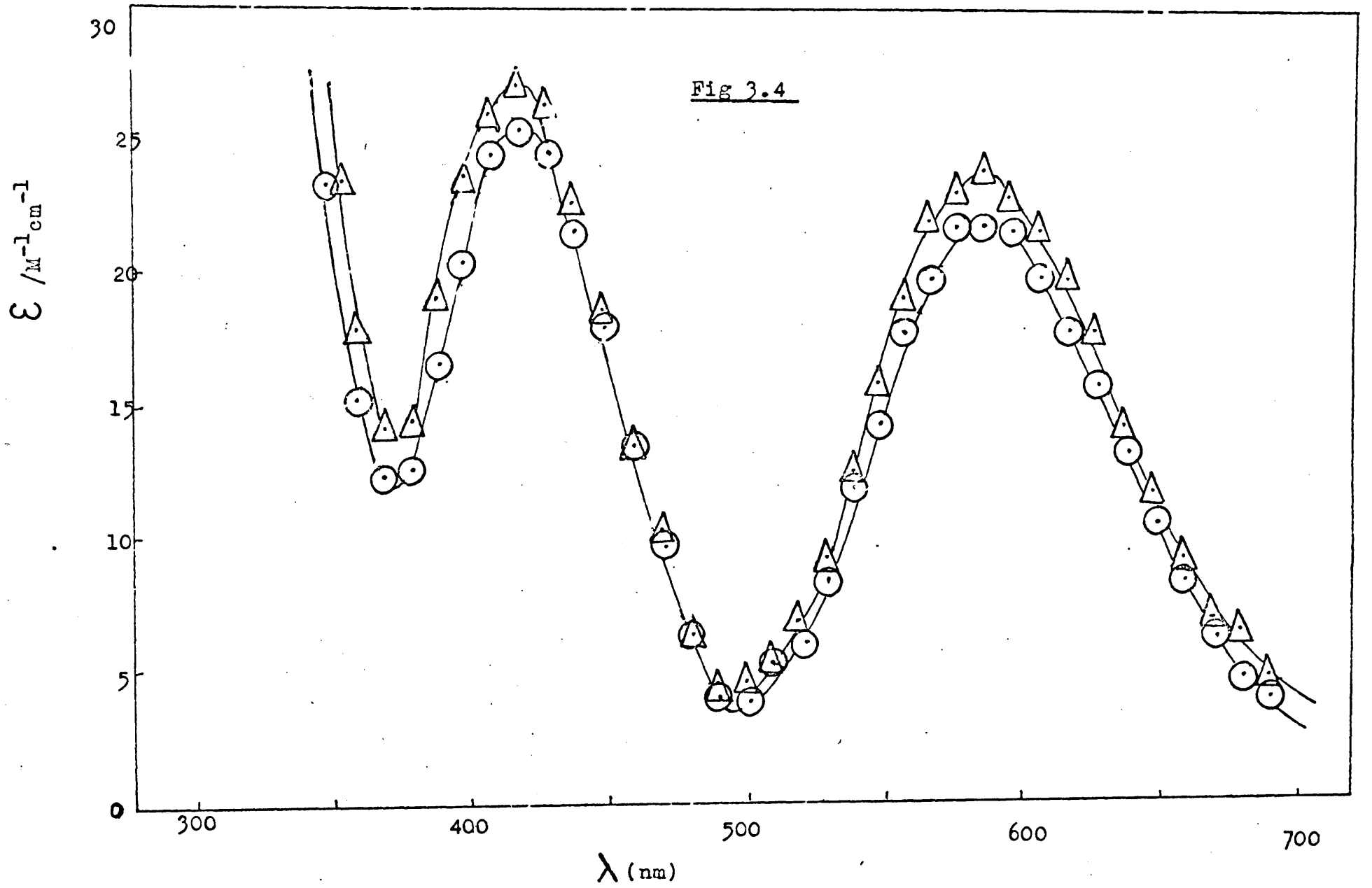
$$(NH_2)_2CS + Ag^+ + 2NH_3 \longrightarrow H_2N.CN + Ag_2S + 2NH_4^+ \quad (2)$$

Repeated determinations indicated that 3.8±0.1 mol of thiourea reacted per mole of chromium (VI) and since 3 mol were oxidised to the disulphide, the remainder is considered to be

bound in the inert chromium (III) complex. Some disulphide may be weakly bound in the complex ion since sulphur analyses of ion-exchange eluates based on SO_4^{2-} (see chapter I) indicated high S : Cr ratios. The chromium content of the separated fractions was determined by bromine oxidation in basic media in a manner described in chapter I. In this way, the relative proportions of two +3 product ions were characterised as $[Cr(H_2O)_6]^{3+}$ (35%) and $[(H_2O)_5 Cr\{(NH_2)_2 CS\}]^{3+}$ (59-62%). The small band of more highly charged (> 4+) material retained on the column thus amounted to < 5% of the initial chromium ion, and may also have some thiourea co-ordinated.

The formulation of a 1:1 chromium (III) - thiourea complex is thus consistent with the earlier observation of 0.8 ± 0.1 mol reductant co-ordinated, although the possibility of a 1:2 complex being present cannot be completely eliminated. The spectrum of the sulphur containing fraction (fig 3.4) was obtained (after separation on the column) by elution with ~5M sodium perchlorate containing 0.1M $HClO_4$. In this way solutions ~ 0.01M in complex ion were prepared.

A similar procedure adopted for the ethylenethiourea reaction revealed the existence of three products one of which was more readily eluted from the column. Reaction of the excess of ethylenethiourea in a manner similar to that described above resulted in quantitative precipitation



Spectra of N-bonded 1:1 Cr^{III} - thiourea products: (⊙), thiourea; (△), NN^{1}-ethylenethio-urea

of the 1:1 silver (1)-ethylenethiourea complex. The excess of silver ion was then titrated against NH_4NCS. Repeated determinations revealed a retention of 0.6 ± 0.1 mol of reductant per mole of chromium (III) produced. Only two of the fractions showed significant amounts of sulphur to be present, the third being identified as $[Cr(H_2O)_6]^{3+}$ (~30%). Again small amounts of highly charged species were not eluted.

Comparison of the chromium (III) content and co-ordinated reductant figures suggest that two isomeric forms of the 1:1 complex are formed and the first fraction (~15%) is considered to be the S - bonded isomer $[(H_2O)_5 Cr^{III}(\overline{SC;NH.CH_2.CH_2.NH})]$ in which there is substantial charge separation if protonation of one of the ring nitrogen atoms takes place in acidic media. The third fraction (44-48%) (fig. 3.4) is then thought to be the N-bonded isomer similar to the major reaction component of the unsubstituted thiourea system. The possible formation of the S-bonded isomeric species which undergoes ready hydrolysis may result from steric hindrance of the substituted reductants.

Attempts were made to further identify the green complexes formed. After elution from the ion-exchange column, the solution was concentrated on a rotary evaporator. In this way the $NaClO_4$ was separated and the chromium (III) complex redissolved in diethyl ether containing the minimum amount of methanol. Repeated reduction to a solid followed by extraction gave a green

Solution which when finally dried at reduced pressure over P_2O_5 yielded a purple solid. When the redox reaction with thiourea was carried out in chloride media. Some $[CrCl]^{2+}$ (~10%) was formed and, using the method described above, the purple compound $[Cr(H_2O)_5\{(NH_2)_2CS\}]Cl_3$ HCl was produced (Found: C,4.6; Cl,40.9; Cr,14.2; N,7.8. Calculated: C,3.3; H,4.2; Cl,39.3; Cr, 14.4; N, 7.8%.).

These purple solids are extremely hygroscopic and readily revert to the green solutions. The isolation of these species thus confirms the ion-exchange results that the cationic species produced are $[Cr(H_2O)6]^{3+}$ and $[Cr\{(NH_2)_2CS\}]^{3+}$ respectively.

RESULTS AND DISCUSSION

(a) The complex intermediates

Studies were made at a wavelength of 380nm and the presence of complexes was confirmed from initial optical density measurements. From data where the hydrogen - ion concentration was varied, it was observed that the extent of complex formation depended on the amounts of hydrogen ion present. If L = Substrate, the initial rapid reactions may be represented as (3).

$$[(HO)CrO_3]^- + H^+ + L \rightarrow [LCrO_3] + H_2O \qquad (3)$$

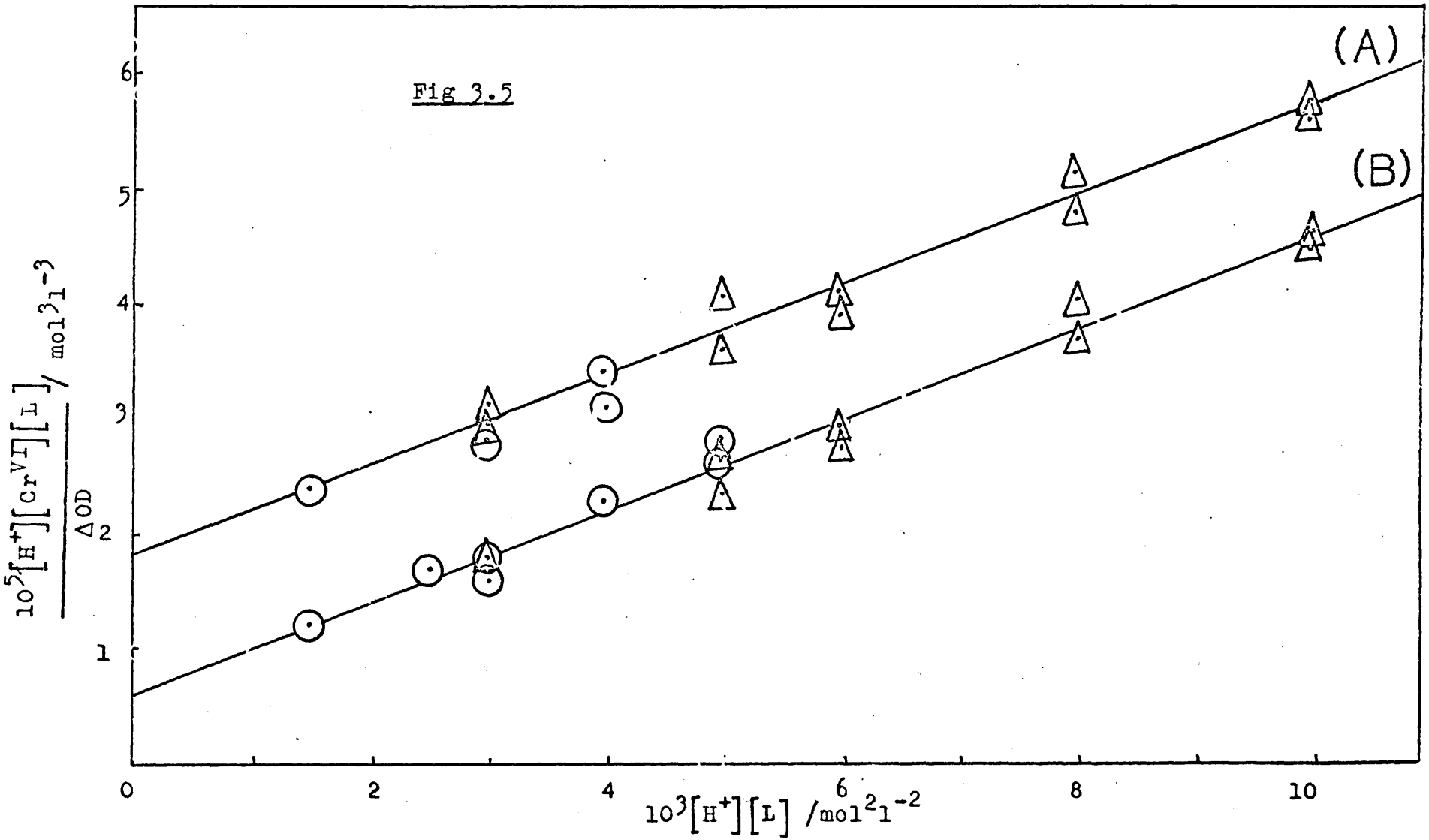
and at the wavelength used where both the uncomplexed and complex forms of chromium (VI) absorb equation (4) may be

written[70,104] as

$$\frac{[Cr^{VI}]_T[L][H^+]}{\Delta OD} = \frac{[L][H^+]}{\Delta\varepsilon . l} + \frac{1}{K.\Delta\varepsilon.l} \qquad (4)$$

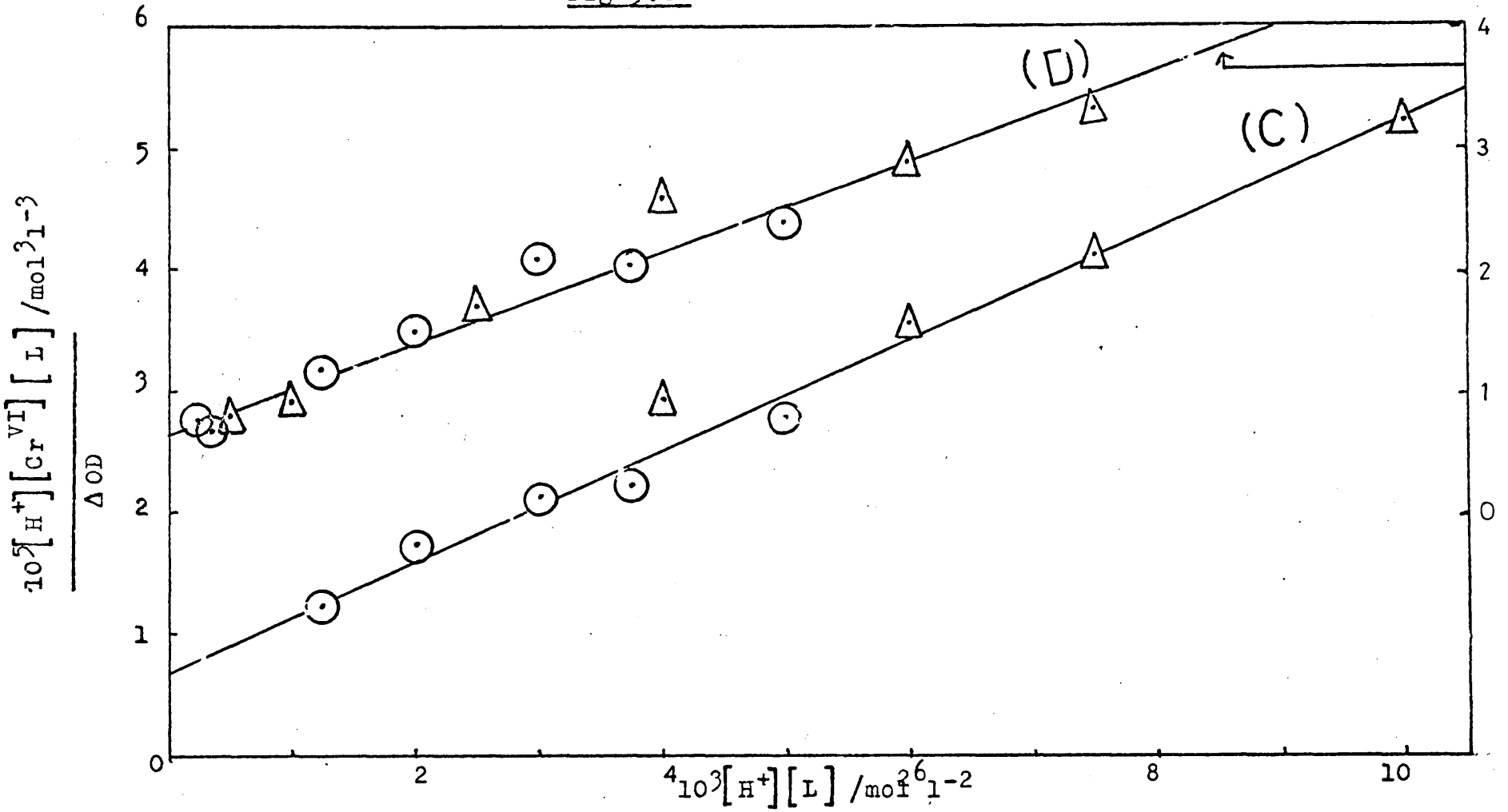
where $[Cr^{VI}]_T$ = the total metal - ion concentration, ΔOD = the difference in absorbance between the complex and Cr^{VI}, $\Delta\varepsilon$ = the corresponding difference in absorption coefficients, and l = the path-length (0.5cm). The data in figures 3.5 and 3.6 represent some of the initial optical density changes presented in the form of equation (4) from which both the equilibrium constants and the absorption coefficients may be derived. Details of these constants derived at each temperature studied are presented in Table 3.1 where little temperature variation of the absorption coefficient is observed.

A similar complex formation has been observed[117] in the case of the thiocyanate ion and the K values of 380, 211, 570 and 700 $l^2\ mol^{-2}$ for thiourea, ethylene thiourea, N-methyl thiourea and NN^{1}dimethyl thiourea respectively may be compared with that of 220 $l^2\ mol^{-2}$ derived previously for thiocyanate [104] (I = 0.3M). The corresponding value for $[CrO_3Cl]^-$ formation is 17 $l^{-2}\ mol^{-2}$ (ref 107). There are available few data with which the thermodynamic parameters may be compared. For the formation of the thiosulphato-complex, $[CrO_3(S_2O_3)]^{2-}$, a value of ΔH, - 3 k cal mol^{-1} has been derived,[92] but more information is clearly required before conclusions can be drawn as to the significance of such values.



Plots of the left-hand side of equation (4) against $[H^+][L]$ for thiourea at 15.2°C (A) and NN^1-ethylenethiourea at 24.9°C (B) $[H^+]$ = 0.5M (⊙) and 1.0M (Δ) respectively.

Fig 3.6



Plots of the left-hand side of equation (4) against $[H^+][L]$ for NN^1-dimethylthiourea at 25°C (C) (D); $[H^+]$ = 0.25M (0) and 0.50M (Δ) respectively.

and N-Methylthiourea at 25°C

TABLE 3.1

Thermodynamic parameters for initial complex formation derived using equation (4)

L = Thiourea

$T^{o}C$	15.2	20.0	24.9	30.0	35.0
$K\ l^{2}mol^{-2}$	648±120	481±100	380±60	280±45	215±40
$\varepsilon\ l\ mol^{-1}cm^{-1}$	1256	1230	1270	1250	1254

ΔG = -3.52±0.3k cal.mol^{-1}, ΔH = -9.8±0.6K.cal mol^{-1}

ΔS = -21.0±3 cal $K^{-1}mol^{-1}$

L = NN^{1} - ethylenethiourea

$T^{o}C$	15.2	20.0	24.9
$K\ l^{2}\ mol^{-2}$	361±18	256±30	211±15
$\varepsilon\ l\ mol^{-1}cm^{-1}$	1232	1238	1263

ΔG = -3.2±0.4 k cal.mol^{-1}, ΔH = -8.8±0.9 k cal.mol^{-1}

ΔS = -19±4 cal K^{-1} mol^{-1}

L = N - methyl thiourea

$T^{o}C$	15.0	20.0	25.0
$K\ l^{2}\ mol^{-2}$	603±123	598±125	569±120
$\varepsilon\ l\ mol^{-}cm^{-1}$	1231	1200	1290

L = NN^{1} - dimethyl thiourea

$T^{o}C$	20.0	25.0
$K\ l^{2}\ mol^{-2}$	800±30	708±50
$\varepsilon\ l\ mol^{-1}cm^{-1}$	1205	1200

It is also of interest to note that in the present investigation the charge-transfer maxima (fig3.1) are at 380nm similar to that for the thiosulphate complex, $[CrO_3(S_2O_3)]^{2-}$ ref (110 and 116) and identical to that for the thiocyanate species[117] (380nm) suggesting a common mode of co-ordination to the chromium centre. Also the equilibrium constants, K, in these reactions are of the same order of magnitude; this would tend to eliminate the possibility of an attachment through the nitrogen atoms since the steric hindrance involved in the case of the substituted molecules might be expected to be much more significant.

(b) Kinetics of the oxidation reactions

The first order decrease in absorbance at 380nm was observed to be both ligand and hydrogen-ion dependent, although non-integral in order with respect to both. Rate constants at 420nm in the lower ligand-concentration range were in satisfactory agreement with those at 380nm. Two differing hydrogen-ion dependences were observed in these oxidation reactions depending on the thiourea substrate.

The reaction with thiourea is considered to proceed via three paths which may be written in overall form as (5) - (7),

$$(O_3Cr\ L) \xrightarrow{k_0} Cr^{V} + L^{\bullet} \qquad (5)$$

$$(O_3CrL) + H^{+} + L \xrightarrow{k_1} Cr^{IV} + L^{1}\text{-}L^{1} \qquad (6)$$

$$(O_3CrL) + 2H^{+} + L \xrightarrow{k_2} Cr^{IV} + L^{1}\text{-}L^{1} \qquad (7)$$

$$2L^{\cdot} \underset{\text{fast}}{\rightleftharpoons} L^1\text{-}L^1 \qquad (8)$$

and a rate law consistent with a scheme of this type may be expressed as (9) conforming to the observed first - order rate behaviour

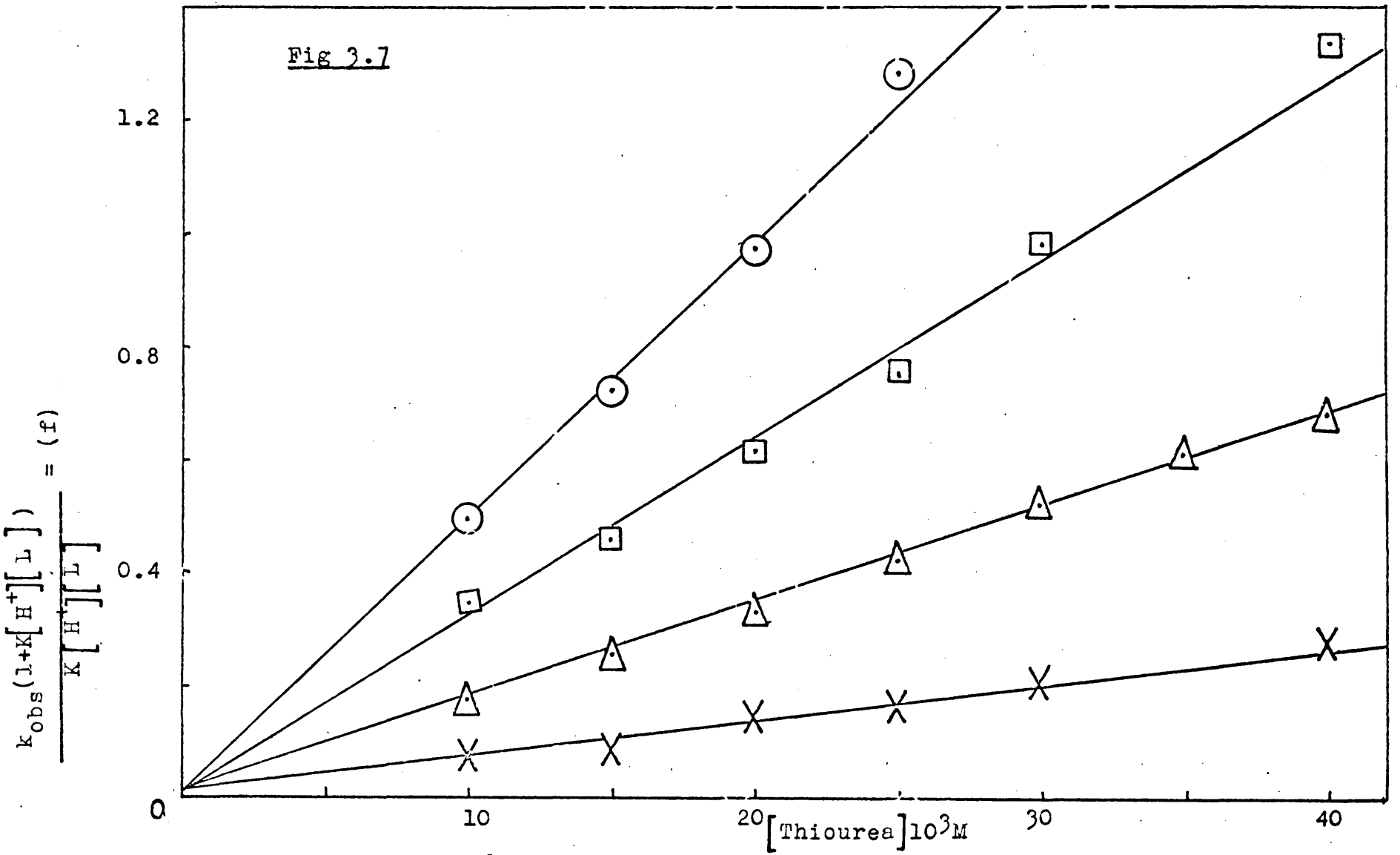
$$\text{Rate} = -\frac{d[Cr^{VI}]}{d_t} = \frac{K[H^+][L]\left(k_0 + k_1[H^+]^2[L]\right)[Cr]_T}{(1 + K[L][H^+])} \qquad (9)$$

Rearrangement of the observed rate constant, kobs, leads to equation (10)

$$\frac{kobs\ (1 + K[L][H^+])}{K[L][H^+]} = (f) = k_0 + [H^+][L](k_1 + k_2[H^+]) \qquad (10)$$

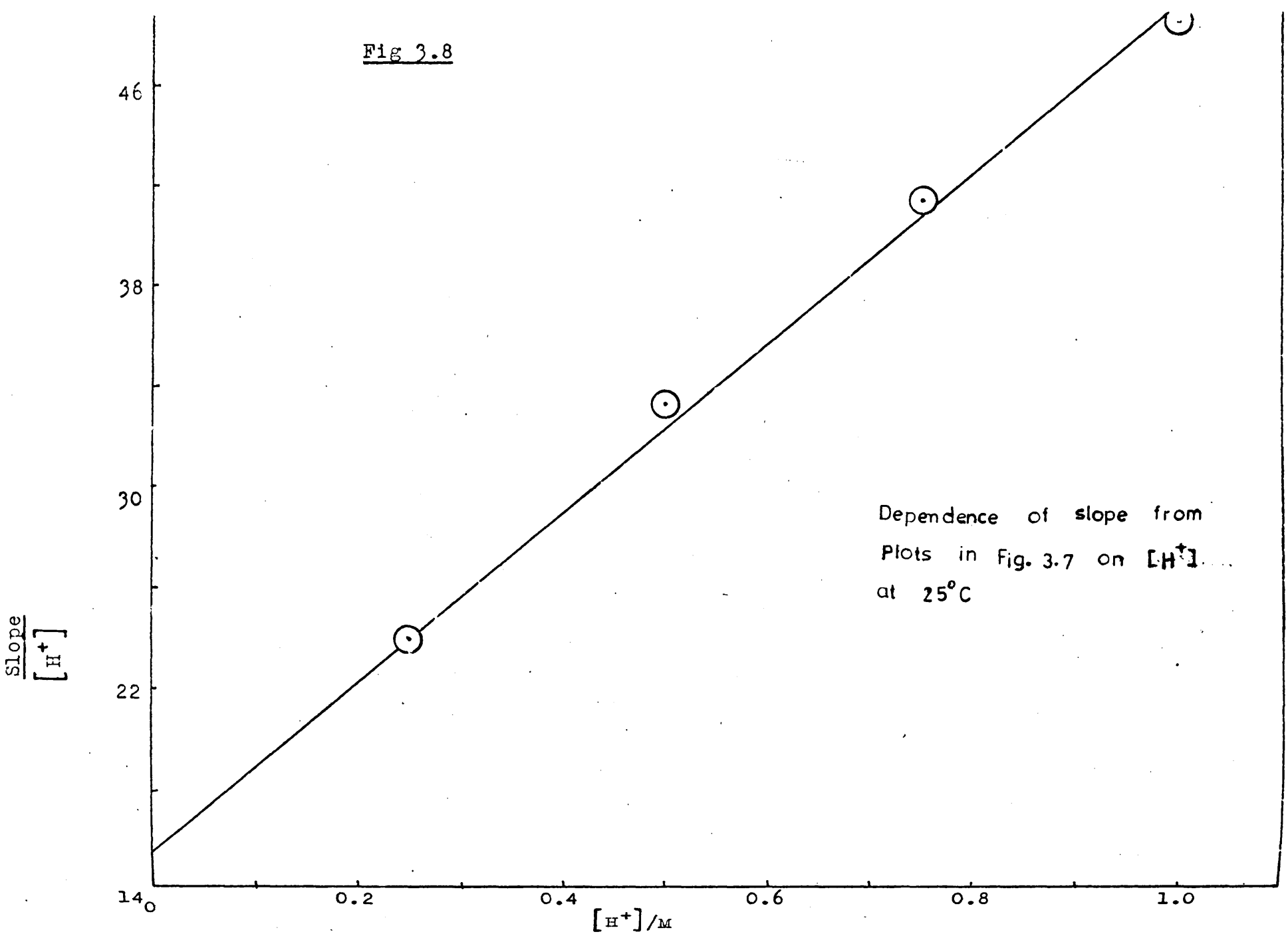
From a knowledge of the equilibrium constants, the left hand side of equation (10) was evaluated (f) and a straight line obtained on plotting (f) against [L] (fig 3.7) yielded k_0. From the hydrogen - ion dependence of such plots (Fig 3.8) k_1 and k_2 were derived (Table 3.2). A fuller representation of the reaction paths is provided in the scheme (vide infra).

From the initial optical - density changes it is known that one proton is required in the formation of the complexes, The k_0 path is postulated as a one - electron reduction of chromium (VI). In the other studies involving redox processes of this type it has been observed that two protons are required[29,90,129] except in the reaction of VO^{2+} where two protons are released on oxidation.[114] If the one - electron half reaction for thiourea is written



Plots of (f) against thiourea at 25°C (equation 10). (X), $[H^+]$ = 0.25M; (▲), $[H^+]$= 0.5M: (▣), $[H^+]$ = 0.75M; (⊙)$[H^+]$ = 1.0M; I = 1.0M.

Fig 3.8


46
38
30
22
14
0
0.2
0.4
0.6
0.8
1.0
Slope / [H+]
[H+]/M
Dependence of slope from Plots in Fig. 3.7 on [H+] at 25°C

SCHEME 1

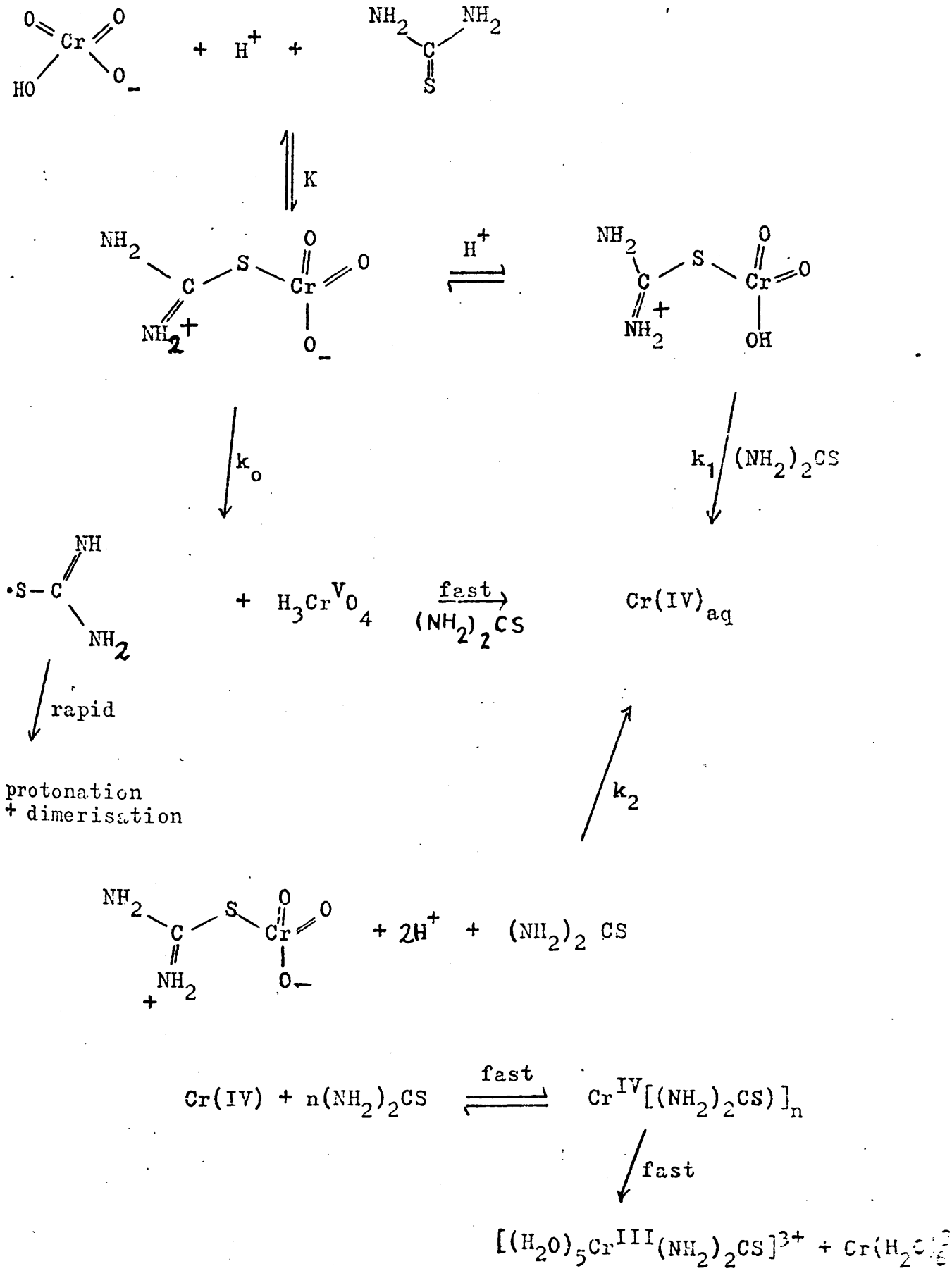

+ H+ +
K
H+
k0
k1 (NH2)2CS
rapid
+ H3CrVO4
fast
(NH2)2CS
Cr(IV)aq
protonation
+ dimerisation
k2
+ 2H+ + (NH2)2 CS
Cr(IV) + n(NH2)2CS
fast
CrIV[(NH2)2CS)]n
fast
[(H2O)5CrIII(NH2)2CS]3+ + Cr(H2O
~65-70%
~25-30%

TABLE 3.2

Rate constants for the reactions of chromium (VI) with thiourea and its N-substituted thioureas.

L - Thiourea

$T^{o}C$	k_o l^2 $mol^{-2}s^{-1}$	k_1 l^2 $mol^{-2}s^{-1}$	k_2 $l^3mol^{-3}s^{-1}$
15.2	0.005±0.005	8.6±1.8	29±6
20.3	0.015±0.01	10.0±1.5	31±3
24.9	0.020±0.01	15.6±1.4	33±2
30.0	0.030±0.01	19.6±1.6	33±2
ΔH^* kcal mol^{-1}		10.7±2.5	1
ΔS^* cal K^{-1} mol^{-1}		19.0±8	-45±6

L = NN^1- Ethylenethiourea

T^oC	k_α s^{-1}	k_β l^3 mol^{-3} s^{-1}
15.2	0.12±0.01	37.0±2.0
20.0	0.20±0.03	46.5±4.0
24.9	0.30±0.04	47.5±4.0
ΔH^* k cal mol^{-1}	15±1	1.5
ΔS^* cal K^{-1} mol^{-1}	-9±3	-45±5

L = N-Methylthiourea

T^oC	k_α s^{-1}	k_β l^3 $mol^{-3}s^{-1}$
15.0	0.010±0.001	59±3
20.0	0.015±0.003	61±4
25.0	0.020±0.005	66±5
ΔH^* kcal mol^{-1}		1.7
ΔS^* cal mol^{-1} K^{-1}		-45±7

L = NN^{1}-Dimethylthiourea

T°C	k_{α} s^{-1}	k_{β} l^{3} mol^{-3} s^{-1}
20.0	0.004±0.002	31±3
25.0	0.010±0.005	34±4

as, $(NH_2)_2CS \rightleftharpoons NH_2 \cdot NH : C.S. + H^+ + e^-$ (11)

then the second proton is derived from the substrate itself thus satisfying the formal hydrogen - ion requirements.

Although this path constitutes only a minor route, confirmation of the formation of radicals has been derived from acrylonitrile polymerisation, and a weak electron resonance signal was observed at 77K (at X - band frequency), g = 2.002±0.002. This is consistent neither with solely a d^1 chromium (V) complex (expected $g = 1.98$[130]) and it may arise from the formation of a chromium (V) complex with an uncharged thiourea molecule acting as a ligand. The magnitude of the signal confirms that the principal paths are probably two - electron steps involving 2 moles of reductant. In the case of the k_2 path, the hydrogen - ion dependence parallels that of the k_0 route in that there may be formation of a complex of the type $CrO_2(thiourea)_2$ analogous to the species CrO_2Cl_2 and CrO_2F_2. The construction of models in which the ligands are sulphur bonded for all the reductants indicate that structures of this type are feasible and may be considered as transition states. (see Fig 4.16, Chapter IV)

In the case of other N-substituted thioureas there was no evidence for a reaction corresponding to equation (6) and two formal reaction paths were detected,

$$(O_3Cr\ L) \xrightarrow{k_\alpha} Cr^{V} + L^{\cdot} \qquad (12)$$

$$(O_3Cr\ L) + 2H^{+} + L \xrightarrow{k_\beta} Cr^{IV} + L^{1}\text{-}L^{1} \qquad (13)$$

$$2\ L^{\cdot} \underset{\text{fast}}{\rightleftharpoons} L^{1}\text{-}L^{1} \qquad (14)$$

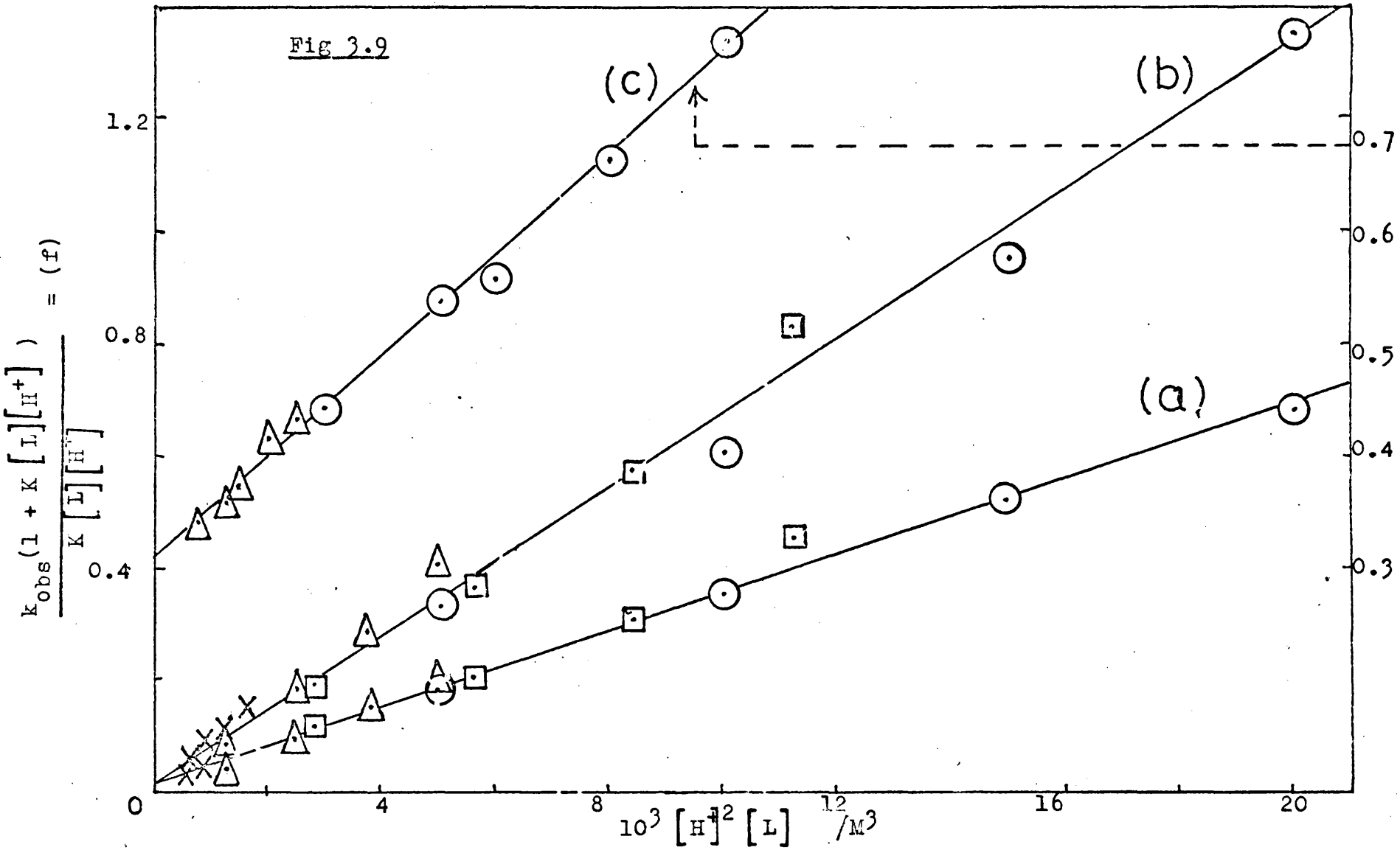
and the rate law may be written as in (15).

$$-\frac{d[Cr^{VI}]}{dt} = \frac{K[L][H^{+}]\left(k_\alpha + k_\beta[H^{+}]^2[L]\right)[Cr^{VI}]_T}{(1 + K[L][H^{+}])} \qquad (15)$$

Treatment of the data in a manner similar to that for thiourea yielded the rate constants k_α and k_β (Table 3.2) in thiourea yielded the rate constants k_α and k_β (Table 3.2) which these values were evaluated are shown in Fig 3.9.

The experimentally derived kinetic data are presented in Table 3.3 where comparison may be made with the calculated first - order rate constants equations (9) and (15) derived from the data in Tables 3.1 and 3.2 and where the overall agreement is considered good. The reaction paths k_α and k_β are then analogous to those (k_o and k_2) depicted in the scheme and the possibility of a transition state of the type (CrC_2L_2) in the latter reaction may be considered.

The rate laws observed differ only relatively slightly from those derived previously in oxidations of this type.[101,110, 117,132] and then only at low ligand concentrations. At the higher concentrations of all the thiourea substrates, the predominant paths k_2 and k_β are directly comparable to the route proposed in the thiocyanate study.[117] Also the composite rate constants k_2 = 34 (thiourea), k_β = 47



Plots of (f) against $[H^+]^2[L]$ at 25°C for (a), NN^1-dimethyl thiourea; (b), N-methylthiourea and (c), NN^1-ethylenethiourea; $[H^+]$ = 0.25M (X), 0.50M (Δ), 0.75M (⊟) and 1.0M (⊙).

TABLE 3.3

Comparison of observed and calculated rate constants [equation (10)] at various ligand and hydrogen-ion concentrations.

I = 1.0M and λ = 380nm.

L = Thiourea

Temp. = 30.0° $[Cr(VI)]_t = 4 \times 10^{-4}M$

$[H^+] = 0.25M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
10.0	0.038	0.041
15.0	0.0633	0.069
20.0	0.097	0.099
25.0	0.129	0.1298

$[H^+] = 0.50M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0573	0.050
10.0	0.135	0.133
15.0	0.202	0.2037
20.0	0.286	0.288
25.0	0.392	0.374

$[H^+] = 0.75M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
10.0	0.268	0.246
15.0	0.424	0.401
20.0	0.560	0.562
25.0	0.760	0.724
30.0	0.890	0.8874

$[H^+] = 1.0M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
10.0	0.401	0.410
15.0	0.636	0.662
20.0	0.930	0.918
25.0	1.190	1.177
30.0	1.430	1.437

Temp. = 24.9° $[Cr(VI)]_t$ = (2-4) x 10^{-4}M

$[H^+]$ = 0.50M			$[H^+]$ = 1.0M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$	$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
3.0	0.0282	0.025	3.0	0.109	0.0894
5.0	0.0512	0.049	5.0	0.177	0.1750
6.0	0.0613	0.0625	6.0	0.222	0.2195
8.0	0.0820	0.090	8.0	0.295	0.3118
10.0	0.1160	0.119	10.0	0.390	0.406
15.0	0.1880	0.195	15.0	0.612	0.646
20.0	0.2640	0.273	20.0	0.860	0.889
25.0	0.3480	0.352	25.0	1.160	1.133
30.0	0.444	0.431	30.0	1.360	1.378
35.0	0.540	0.511	35.0	1.590	1.623
40.0			40.0	2.040	1.869

$[H^+]$ = 0.25M			$[H^+]$ = 0.75M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$	$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
10.0	0.038	0.039	10.0	0.256	0.242
15.0	0.0496	0.0647	15.0	0.370	0.389
20.0	0.094	0.092	20.0	0.516	0.539
25.0	0.115	0.119	25.0	0.656	0.689
30.0	0.156	0.148	30.0	0.880	0.841
40.0	0.214	0.206	40.0	1.230	1.146

Temp. = 20.3°

$[H^+]$ = 0.25M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0132	0.0139
10.0	0.0296	0.032
15.0	0.0492	0.052
20.0	0.0692	0.0728
25.0	0.099	0.094

$[H^+]$ = 0.50M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0456	0.043
10.0	0.100	0.0998
15.0	0.171	0.160
20.0	0.228	0.2215
25.0	0.318	0.271

$[H^+]$ = 0.75M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
10.0	0.214	0.205
15.0	0.324	0.325
20.0	0.444	0.446
25.0	0.572	0.568
30.0	0.760	0.773

$[H^+]$ = 1.0M		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
2.5	0.0744	0.0635
3.75	0.121	0.1074
5.0	0.154	0.154
6.25	0.210	0.207
7.50	0.250	0.2496
8.75	0.296	0.298
10.0	0.350	0.348
15.0	0.720	0.747

Temp. = 15.0°

$[H^+] = 0.25M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0112	0.0111
10.0	0.0276	0.0276
15.0	0.046	0.0456
20.0	0.0656	0.0644

$[H^+] = 0.50M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
3.0	0.0215	0.0195
5.0	0.0387	0.0388
6.0	0.0452	0.049
8.0	0.0636	0.0703
10.0	0.092	0.092
15.0	0.157	0.150

$[H^+] = 0.75M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0812	0.0842
10.0	0.194	0.193
15.0	0.334	0.305

$[H^+] = 1.0M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
3.0	0.082	0.078
5.0	0.144	0.147
6.0	0.176	0.183
8.0	0.234	0.256

L = Ethylenethiourea

Temp. = 15.2° $[Cr(VI)]_t = 2 \times 10^{-4}M$

$[H^+] = 0.50M$			$[H^+] = 1.0M$		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$	$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
3.0	0.0488	0.0519	3.0	0.122	0.120
5.0	0.078	0.079	5.0	0.193	0.196
6.0	0.094	0.091	6.0	0.231	0.234
8.0	0.120	0.115	8.0	0.296	0.309
10.0	0.143	0.137	10.0	0.380	0.384

$[L] = 7.5 \times 10^{-3}M$

$[H^+]$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
0.25	0.0524	0.0554
0.35	0.752	0.075
0.50	0.115	0.109
0.60	0.142	0.136
0.80	0.216	0.204
1.00	0.278	0.296

Temp. = 20.0° $[Cr(VI)] = 4 \times 10^{-4}M$

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.244	0.243
7.5	0.338	0.361
10.0	0.484	0.478
12.5	0.568	0.595
15.0	0.704	0.712
17.5	0.880	0.829
20.0	0.94	0.945
25.0	1.270	1.18

Temp. = 24.9° $[Cr(VI)]_t = 2 \times 10^{-4}M$

$[H^+] = 0.50$			$H^+ = 1.0M$		
$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$	$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
3.0	0.082	0.081	3.0	0.173	0.172
5.0	0.122	0.124	5.0	0.276	0.276
6.0	0.146	0.144	6.0	0.310	0.327
8.0	0.192	0.181	8.0	0.416	0.427
10.0	0.220	0.215	10.0	0.524	0.526

Temp. = 24.9°

[L] = 2.5×10^{-3}M

$[H^+]$M	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
0.25	0.0356	0.0358
0.35	0.0476	0.049
0.50	0.0653	0.0688
0.60	0.092	0.082
0.80	0.118	0.112
1.00	0.151	0.145

[L] = 7.5×10^{-3}M

$[H^+]$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
0.25	0.092	0.091
0.35	0.128	0.122
0.50	0.194	0.172
0.60	0.222	0.209
0.80	0.310	0.295
1.00	0.440	0.402

L = N-Methylthiourea

Temp. = 15.0° [Cr(VI)] = 4×10^{-4}M

$[H^+]$ = 0.25M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0128	0.0122
8.0	0.0224	0.0216
12.0	0.0396	0.0349
15.0	0.0540	0.0453

$[H^+]$ = 0.50M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.045	0.0503
8.0	0.0888	0.0905
12.0	0.150	0.1465
15.0	0.193	0.1894

Temp. = 20.0° [Cr(VI)] = 4×10^{-4}M

[H⁺] = 0.25M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0140	0.0146
8.0	0.0232	0.0244
12.0	0.0404	0.0390
15.0	0.052	0.0499

[H⁺] = 0.50M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0496	0.0542
8.0	0.082	
12.0	0.155	0.1548
15.0	0.218	0.1993

Temp. = 25.0° [Cr(VI)] = 2×10^{-4}M

[H⁺] = 0.25M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0148	
10.0	0.0344	0.0358
15.0	0.0516	0.0557
20.0	0.0836	0.0758

[H⁺] = 0.50M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0532	
10.0	0.136	0.1369
15.0	0.238	0.2167
20.0	0.348	

[H⁺] = 0.75M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.132	0.1400
10.0	0.294	
15.0	0.496	0.4989
20.0	0.740	

[H⁺] = 1.0M

$[L]10^3$	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.242	0.258
10.0	0.512	0.578
15.0	0.850	0.9040
20.0	1.24	

L = NN^1 - Dimethylthiourea

Temp. = 20.0° [Cr(VI)] = 4 x 10^{-4}M

[H$^+$] = 0.50M

[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0290	0.0285
8.0	0.0492	0.0503
12.0	0.0828	0.0803
15.0	0.115	0.1031

[H$^+$] = 0.75M

[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0652	0.0684
8.0	0.116	0.1184
12.0	0.173	0.1872
15.0	0.246	0.2390

Temp. = 25.0° [Cr(VI)] = 2 x 10^{-4}M

[H$^+$] = 0.25M

[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0092	0.0097
10.0	0.0204	0.0200
15.0	0.0344	0.0304
20.0	0.0492	0.0409

[H$^+$] = 0.50M

[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.0340	0.0335
10.0	0.079	0.0741
15.0	0.122	0.1157
20.0	0.186	0.1577

[H$^+$] = 0.75M

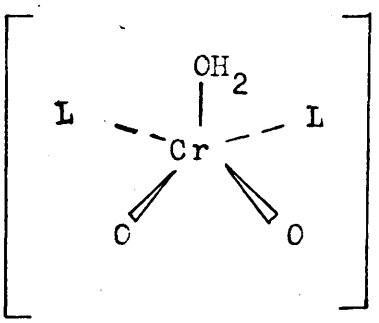
[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.083	0.0767
10.0	0.168	0.1694
15.0	0.272	0.2638
20.0	0.412	0.3587

[H$^+$] = 1.0M

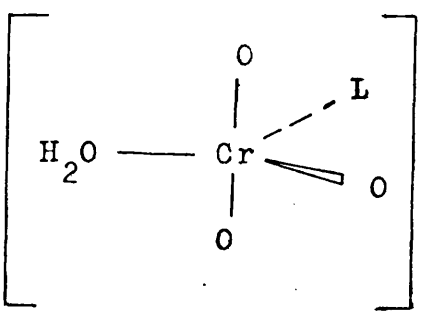
[L]10^3	k_{obs}/s^{-1}	$k_{obs\ calc}/s^{-1}$
5.0	0.138	0.1400
10.0	0.304	0.3067
15.0	0.472	0.4752
20.0	0.632	0.6444

(ethylenethiourea), $k\beta$ = 66 (methyl-thiourea) and $k\beta$ = 32 (dimethyl-thiourea) $l^3\ mol^{-3}\ S^{-1}$ may be compared directly with a value of 10 $l^3\ mol^{-3}\ S^{-1}$ for the corresponding NCS^- reaction. These rate constants are of the same order of magnitude and the lack of any significant kinetic effects in the N - substituted thiourea series may be due to preferred co-ordination of the reductants to chromium (VI) through the sulphur atom. In this respect the data are similar to those observed in the reaction of Cobalt (III) with these reductants[119] and also in the corresponding reaction path involving $MnOH^{2+}aq$[120].

In all the systems referred to previously with similar rate laws, the presence of a second sulphur - containing ligand in the transition state is considered important. The role of the hydrogen ions may be to (doubly) protonate an oxygen atom of the original ($HCrO_4^-$) ion thus allowing an easier access for co-ordination of the second thiourea to give a transition state which may be formulated as either square pyramidal, I or trigonal bipyramidal, II, in configuration.



I



II

Were the H_2O molecule to dissociate rapidly, then tetrahedral ($Cr\ O_2L_2$) would be formed. If, however, the oxygen atom

was only singly protonated, it is still possible for attack by the second molecule of reducing agent which is suggested by the k_1 path for the thiourea reaction. Such a mechanism has also been observed previously in the reaction with thiosulphate[92,116] and with sulphite ion.[101] The driving force for reactions of this type where a second molecule of the substrate is involved may be two fold in that there may be some incipent disulphide formation in the transition states which would result in a more facile two - electron reduction to chromium (VI). Experiements carried out in the presence of manganese (II), which is known[29] to act as a trap for chromium (VI), showed no difference in the rate, indicating an absence of any reaction between chromium (VI) and either chromium (IV) or the products of any chromium (IV) redox reactions.[29] This aspect has been discussed in detail in chapter II.

Under conditions of low ligand concentrations it is considered that reduction of chromium (V) (reaction (5) and (12)) is the rate determining process in accord with the mechanism postulated by King and his co-workers[113] for one - electron reductants.

The fate of the Chromium (IV) is less well identified, but the presence of thiourea ligands in the chromium (III) products is consistent with labile chromium (IV) species rapidly co-ordinating several ligands and undergoing a further one - electron redox reaction with the formation of

a radical which dimerises.

$$Cr^{IV} + nL \underset{\text{fast}}{\rightleftharpoons} (Cr^{IV} Ln) \qquad (16)$$

$$(Cr^{IV} L_n) \underset{\text{fast}}{\rightleftharpoons} (Cr^{III} L_{n-1}) + L^{\cdot} \qquad (17)$$

$$2L^{\cdot} \underset{\text{fast}}{\rightleftharpoons} L^{1}_{2} \qquad (18)$$

There is a change in co-ordination number from the tetrahedral chromium (VI) ion to the octahedral chromium (III) products. The nature of chromium (IV) species in solution is not well documented but it has been postulated that an increase in co-ordination number takes place on formation of chromium (IV). Some support for a labile chromium (IV) species is also given by observations made during the course of this investigation that in chloride media, in the thiourea reaction, some $(Cr\ Cl)^{2+}$ is formed as well as the Cr^{3+} and $[Cr\{(NH_2)_2CS\}]^{3+}$ complexes. Since Cr^{III} is substitution inert, the chloride ion must have been attached to the chromium centre in a higher oxidation state with the whole complex undergoing reduction.

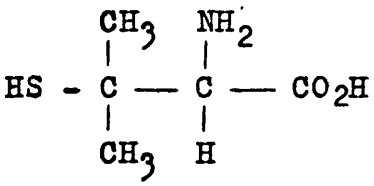
It is of interest that in these systems where there is a large excess of ligand the products are disulphides with no evidence for further oxidation to sulphones.[118,133] In this respect these one - electron reductants resemble the corresponding reaction with cysteine[134] but contrast to that with thiocyanate where sulphate is a product.[117]

C H A P T E R IV

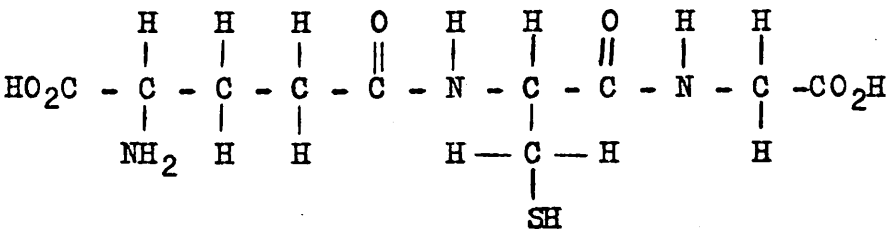
REACTIONS OF CHROMIUM (VI) WITH SOME THIOLS.

Introduction

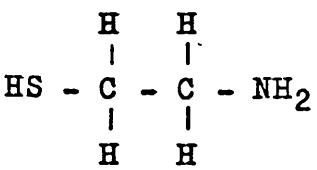
The reactions of chromium (VI) with penicillamine(I), glutathione(II) and β-Mercaptoethylamine(III) shown below, were investigated as part of our continued interest in the reaction of this oxidant with sulphur - containing organic ligands



I



II



III

Unlike thiourea and its N - substituted derivatives, two of these thiols namely penicillamine and glutathione have three different atoms, viz O, N and S available for attachment to metal ions. In all the three cases,

complex formation has been observed to take place prior to redox reactions and it is of interest to investigate whether the bonding modes in these complexes are any different from those observed for similar reactions described in the preceding chapters. The choice of thiols used as reductants in these studies is such as would enable their chelating abilities to be investigated. For example, if oxygen of the carboxylic group is an important co-ordinating site then absence of this in β - mercapto - ethylamine should be reflected in the thermodynamic parameters of the complex formation. The relative positions of the various functional groups and in particular the size of the molecule as a whole are also expected to affect these values.

Earlier investigations of the reactions of these thiols derives from their medical or biological significance. Two different symposia[135,136] were held on glutathione in this connection while DL - penicillamine has been employed in the treatment of Wilson's disease, a metabolic error in which an excess of copper is associated with lesions in the brain and liver[137]. Different workers have studied the reaction of copper (11) ions with penicillamine[138,139] in neutral media. A red-violet complex with λ_{max} at 520nm is formed up to a ligand : copper ratio of 1.3 : 1 giving way to a predominantly yellow species at higher ratios. The infra-red spectrum

of the red-violet complex has been considered as consistent with a mixed - valence chelate complex involving mercapto and amino groups. The reactions of penicillamine with various heavy metal ions have also been extensively studied and characteristic reductive chelate formation similar to that observed with cupric ion has been reported.[140] From these results, the authors suggested that the mixed valence complex formation may be an important form in the course of the elimination of copper with penicillamine.

The reaction of chromium (VI) with penicillamine has previously been investigated[141] at pH7. No detailed mechanism was given but a 1 : 3 chromium (III) penicillamine complex was found upon reduction of chromium (VI) by this ligand. In addition an account was given[141] of the medical significance of this system which in the main deals with the effectiveness of the various chelating agents for the removal of chromium bound to haemoglobin

Under the experimental conditions employed in the present investigation, transient orange species were observed in the reduction of chromium (VI) by these thiols. Unlike the thioureas, however the rates of formation of these complexes were found to be sufficiently slow for a kinetic investigation to be made using the stopped-flow technique.

Experimental

All the three thiols, DL - Penicillamine (Puriss), β - mercaptoethylamine HCl and glutathione were Koch-Light products and were used without further purification. Perchloric acid (A.R.) was used to investigate the effect of hydrogen ions on the rate of the reactions while sodium perchlorate (Fluka puriss p.a.) was the added electrolyte in maintaining the ionic strength constant at 1.0M. Sodium dichromate (B.D.H. Reagent) was used in cases where fairly high concentrations of chromium (VI) were desired i.e. stoicheiometric and final product studies, to prevent the precipitation of potassium perchlorate which would have resulted had the potassium salt been used.

Kinetics

The complex formation reactions between chromium(VI) and both glutathione and β-mercapto-ethylamine were studied using the stopped-flow apparatus described in chapter I which had a dead time of the order of 15 milliseconds. The light source used was a Unicam S.P.500 monochromator. The pseudo-first-order rate constants were derived from oscilloscope traces of transmission curves using a Nova 1200 computer, by the method given in Chapter I.

The corresponding reaction with penicillamine was relatively slower and this together with the redox

reactions was monitored using the hand - driven stopped-flow system also described in chapter I.

For the formation reactions the experimental conditions were carefully chosen such that a state of equilibrium was achieved between the reactants and the intermediate complexes before the redox reactions became important. The concentration of the reactants employed are as follows $[Cr^{VI}] = 2 \times 10^{-4}M$, [Ligand] = $(2 - 8) \times 10^{-3}M$, $[H^+]_o$ = (0.02 - 0.10)M and I = 1.0M. In the redox reactions, essentially the same concentrations were used except that the ligand concentration range was extended to $15 \times 10^{-3}M$ in the case of glutathione. The very slow redox reaction between chromium (VI) and β - mercapto - ethylamine was not investigated.

Stoicheiometry

Earlier investigations of a related ligand (L - Cysteine) with the oxidant carried out in this laboratory[134] reveal a variable stoicheiometry when the latter was determined by spectrophotometric titration. For this reason, and because it was considered desirable to measure the stoicheiometry under conditions related directly to the kinetic data, acidimetric titration of the sulphydryl[142] group was used. This involved mixing 50ml of 0.2M[ligand] with 25ml of $4 \times 10^{-2}M$ [Cr (VI)] and the requisite volumes of sodium perchlorate and perchloric acid to give $[H^+]$ = 0.10M and I = 1.0M.

The mixture was finally diluted to 100ml solution with distilled water. When the reaction was completed, a 50ml sample of this mixture was used to charge a Dowex 50W x 8, 100-200 mesh cation exchange resin described in chapter I. The column was rinsed first with water, then with 0.10M $HClO_4$ and finally with a solution containing 0.10M $HClO_4$ and 1.0M $NaClO_4$ until the first coloured complex had almost reached the lower part of the resin. This is to ensure that all the free ligand had been taken off the column. The fraction collected was made up into a standard solution and aliquots titrated against standard sodium hydroxide after treatment as in ref 142.

Products

Exactly the same conditions and experimental procedure were used as above, for the characterisation of the products. The only difference is that after the free or excess ligand had been taken off the column, elution of the various complex species was carried out using perchloric acid and sodium perchlorate mixtures as described in chapter I. Analysis of the chromium and sulphur contents were also achieved using the methods described in chapter I.

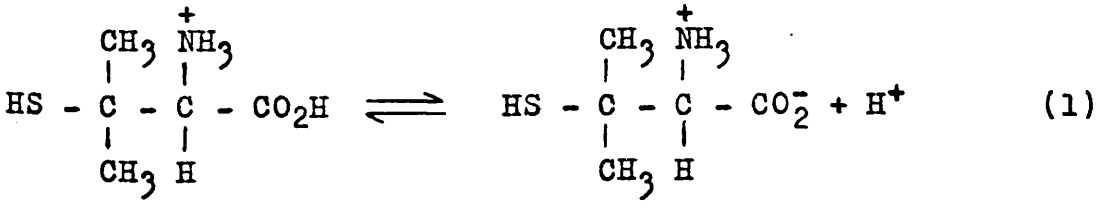
RESULTS AND DISCUSSION

Nature of the reactant species

Interpretation of the kinetic data is strongly dependent on a detailed knowledge of the form of the reactants. Chromium (VI) is known to exist as $HCrO_4^-$ under the experimental conditions used in the present studies. This aspect has been discussed fully in chapters II and III.

The P^{Ka} values corresponding to the loss of a proton by - SH or $\overset{+}{N}H_3$ groups (assuming the latter is protonated) all the ligands are > 8 (ref. 136,139,143,144, 147) whereas those of the carboxylic groups are < 3.5 for the -COOH group in penicillamine the P^{Ka} is 2.44 (ref 147) whereas those of glutathione are 2.1 and 3.5 respectively.[136,144] Hence, under the conditions used in these investigations the zwitterion is presumed to be the dominant species although a small proportion of mono-protonated species may be present.

Dissociation of such protonated species taking penicillamine as an example is given by equation (1)



(1)

and Ka is evaluated using equation (2)

$$Ka = \frac{[H_2RCO_2^-]\ [H^+]}{[\ H_2RCO_2H]} \qquad (2)$$

Attempts were made to determine the effect of these protonated species (if any) on the effective concentrations of the hydrogen ions used. This was done by measuring the pH of the various solutions of the ligand prepared under identical conditions as those used for the kinetic studies. For this purpose a pH meter (ElL Model 23A) was used with a calomel electrode as reference in conjunction with a glass electrode. The pH of the mixed solutions were also determined. The results obtained (Table 4.1) were compared with a calibrated curve (fig 4.1) derived from measuring the pH of various accurate dilutions of perchloric acid containing hydrogen ion concentration (0.01 - 0.10)M again with each solution maintained at 1.0M ionic strength. There was virtually no difference between the two results. Interestingly, no trend was also observed contrary to expectation between the lowest and the highest ligand concentrations used at constant (H^+). Hence, although a small proportion of protonated species, may be formed, the effective concentration of the hydrogen ion is the initial $[H^+]_o$.

TABLE 4.1

Measured pH of the various ligand concentrations containing different $[H^+]_o$ as was used in the kinetic experiments.

L = Penicillamine I = 1.0M

$[H^+]$ = 0.04M

$[Pen]10^3M$	pH Initial	pH Mixture	pH end of Reaction.
2.0	1.08	1.08	1.08
3.0	1.08		
5.0	1.10		
6.0	1.10		
8.0	1.10	1.10	1.10

$[H^+]$ = 0.06M

$[Pen]10^3M$	pH Initial	pH Mixture	pH end of Reaction.
2.0	0.90	0.92	0.92
3.0	0.90		
5.0	0.92		
6.0	0.92		
8.0	0.92	0.92	0.92

$[H^+]$ = 0.08M

$[Pen]10^3M$	pH Initial	pH Mixture	pH end of Reaction
2.0	0.78	0.80	0.80
3.0	0.78		
5.0	0.80		
6.0	0.80		
8.0	0.8	0.80	0.80

$[H^+]$ = 0.10M

$[Pen]10^3M$	pH Initial	pH Mixture	pH end of Reaction
2.0	0.70	0.70	0.69
3.0	0.70		
5.0	0.70		
6.0	0.72		
8.0	0.72	0.70	0.69

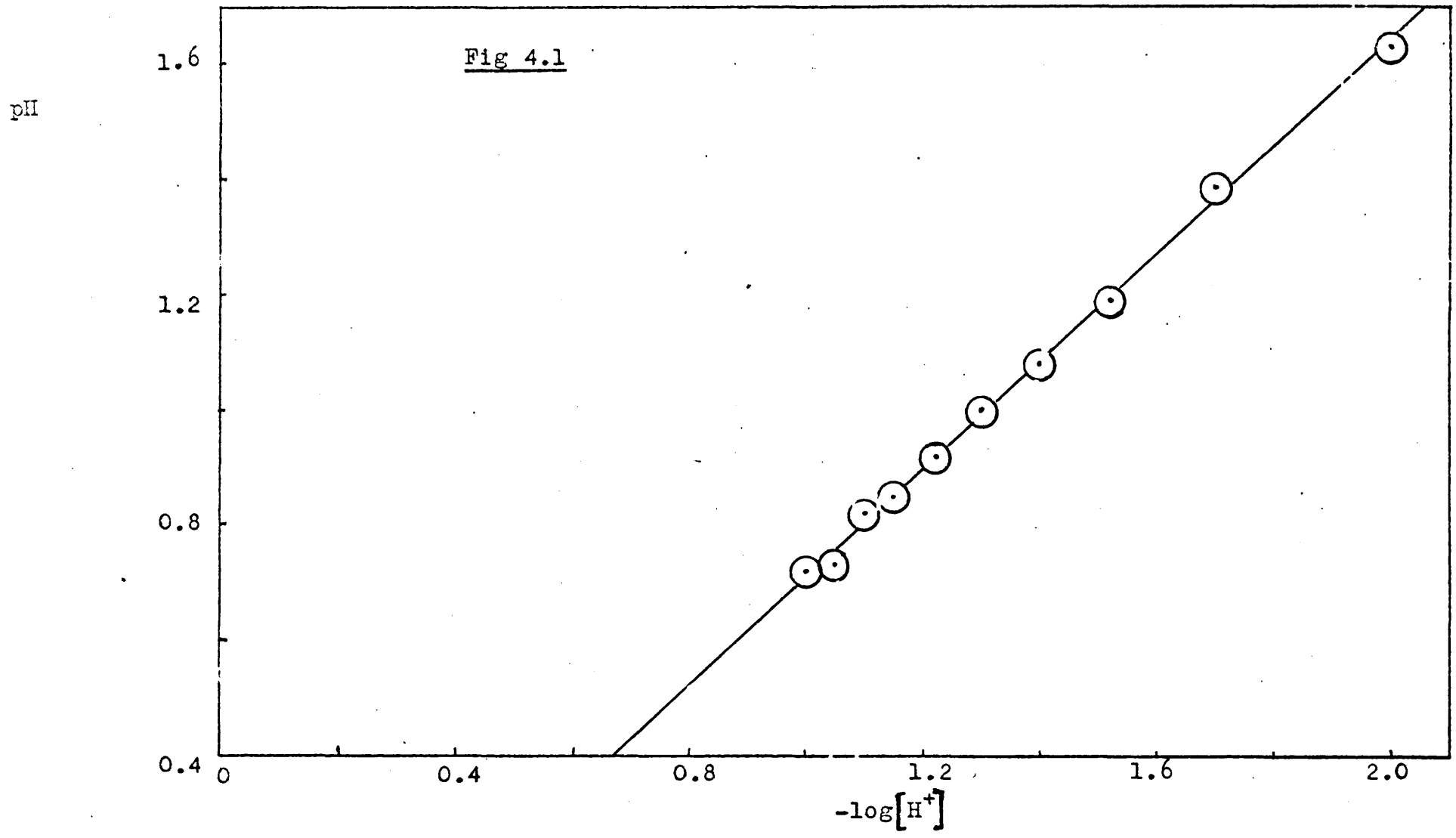
L = Glutathione

[Glutathione] = 2.0×10^{-3}M

$[H^+]_o^M$	pH Initial	pH Mixture	pH end of Reaction
0.04	1.10	1.09	1.10
0.06	0.91	0.91	0.90
0.08	0.79	0.80	0.80
0.10	0.70	0.71	0.71

[Glutathione] = 8.0×10^{-3}M

$[H^+]_o$M	pH Initial	pH Mixture	pH end of Reaction
0.04	1.10	1.09	1.09
0.06	0.92	0.92	0.92
0.08	0.80	0.81	0.82
0.10	0.69	0.70	0.70



Calibration curve: Plot of pH against $-\log_{10}[H^+]$ at 1.0M ionic strength.

Formation of the Intermediate Species

1. Characterisation

(a) Spectrum

In all the kinetic measurements carried out for the determination of the formation rate constants of the intermediate species, the initial absorbance was found to correspond to that of chromium (VI) containing no ligand. In the reactions of chromium (VI) with β-mercaptoethylamine and glutathione which were investigated using the 'fast' stopped flow apparatus described in Chapter I, the change in absorbance ΔOD on attainment of equilibrium is defined by equation (3)

$$\Delta OD = (OD_{max} - OD_0) = \log_{10}\frac{I_{H_2O}}{I_{max}} - \log\frac{I_{H_2O}}{I_{max}} = \log\frac{I_0}{I_{max}} \qquad (3)$$

where I_i is the intensity of light corresponding to ODi. ΔOD can thus be easily calculated from stopped - flow traces. By measuring ΔOD at suitable wavelengths under normal reaction conditions it was possible to obtain the spectrum of the orange species. λ_{max} was found to be 430nm in both cases as shown in Fig 4.2 kinetic and equilibrium measurements were therefore carried out at this wavelength.

Repeated spectroscopic scans of the relatively

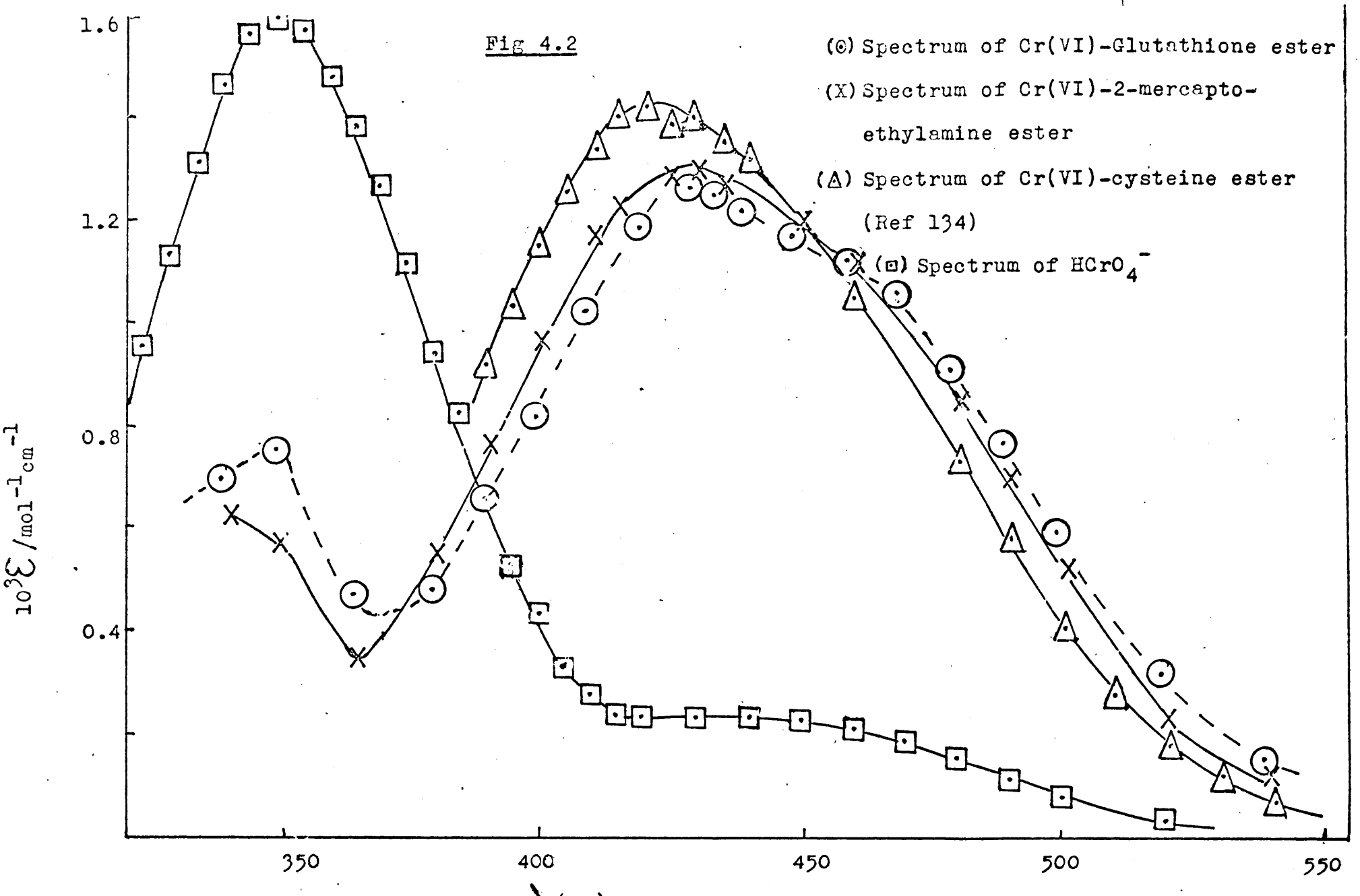


Fig 4.2
(⊙) Spectrum of Cr(VI)-Glutathione ester
(X) Spectrum of Cr(VI)-2-mercapto-ethylamine ester
(Δ) Spectrum of Cr(VI)-cysteine ester (Ref 134)
(⊡) Spectrum of $HCrO_4^-$
$10^3 \varepsilon$ /mol^{-1} l cm^{-1}
1.6
1.2
0.8
0.4
350
400
450
500
550

slowly reacting mixtures of Cr(VI) and penicillamine show a decrease in absorbance at λ = 350nm and an increase at $\lambda \sim 420$nm with an isosbestic point at 390nm (Fig 4.3). This is an indication that the complex exhibits maximum absorption at $\lambda \sim 420$nm. Consequently both the formation as well as the redox of this reaction were studied at λ = 420nm over a hydrogen ion concentration range of (0.02 - 0.10)M

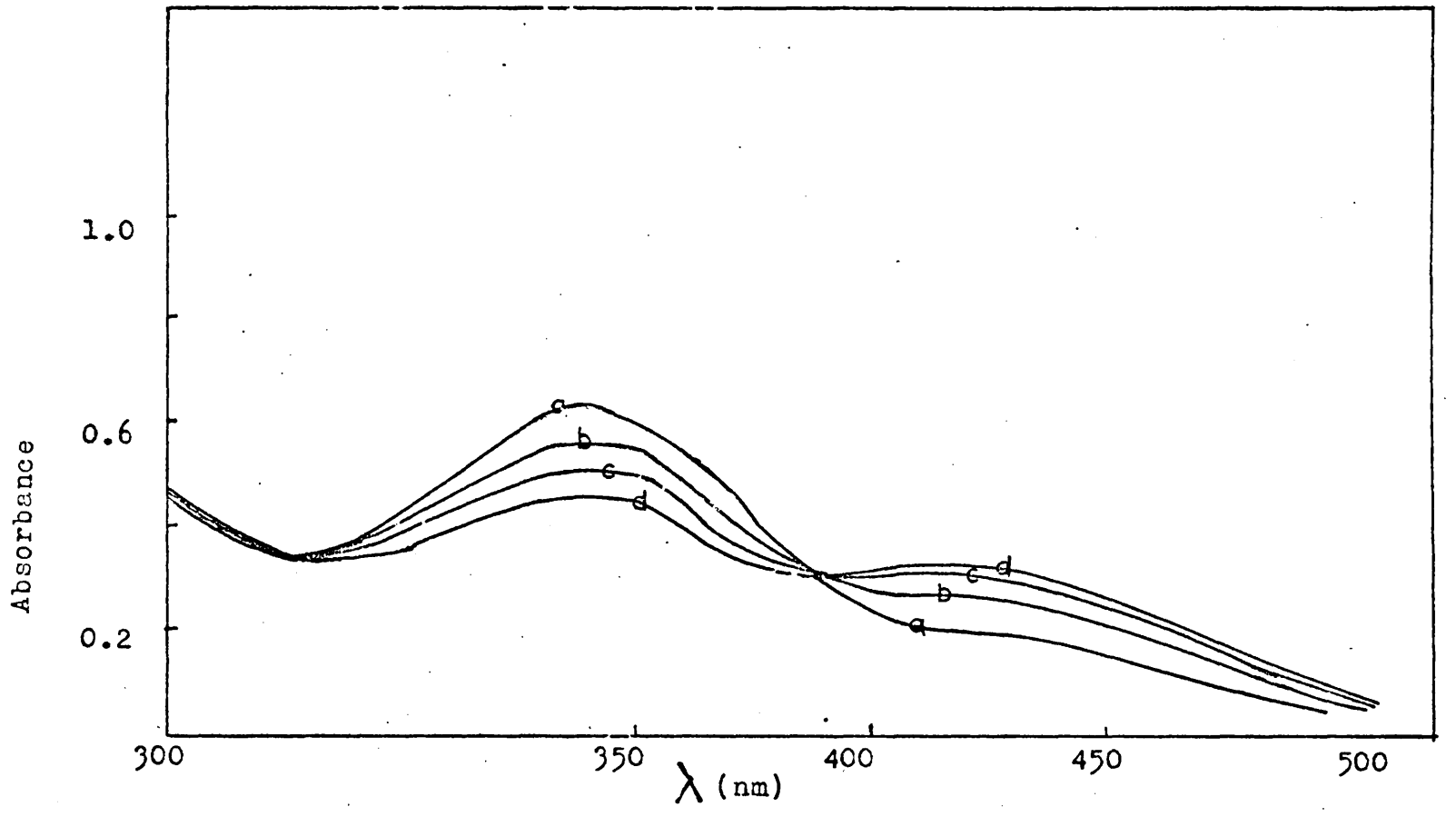
(b) Extinction Coefficients and Equilibrium Constants

A state of equilibrium between the reactants and the complex was observed in all the traces under the experimental conditions employed. On increasing the concentrations of the ligands maintaining in λ $[Cr(VI)]_o$ and $[H^+]_o$ constant, it was discovered that the absorbance OD_{max} did not increase beyond a limiting value which was directly proportional to $[Cr(VI)]_o$. Under such conditions the apparent extinction coefficient ε_{APP} can be obtained using equation (4)

$$\varepsilon_{APP} = \frac{OD_{eqm}}{X \cdot l} \qquad (4)$$

where OD_{eqm} is the absorbance at equilibrium, l is the optical pathlength and x is the concentration of complex present which is itself equal to the $[Cr^{VI}]_o$ initially present. Using this method, ε_{APP} values of 1280±30, 1275±15 and 1265±15 l $mol^{-1}cm^{-1}$ were obtained for the

Fig 4.3



Spectra of slowly reacting mixed solutions of chromium (VI) and penicillamine at, (a), t = 0; (b) t = 2 mins; (c), t = 3 mins; (d), t = 6 mins; $[Cr^{VI}]$ = 4 x 10^{-4}M; [Pen] = 5 x 10^{-3}M; $[H^+]$ = 0.01M I = 1.0M.

extinction coefficients of the complexes formed with penicillamine, glutathione and β-mercapto-ethylamine respectively.

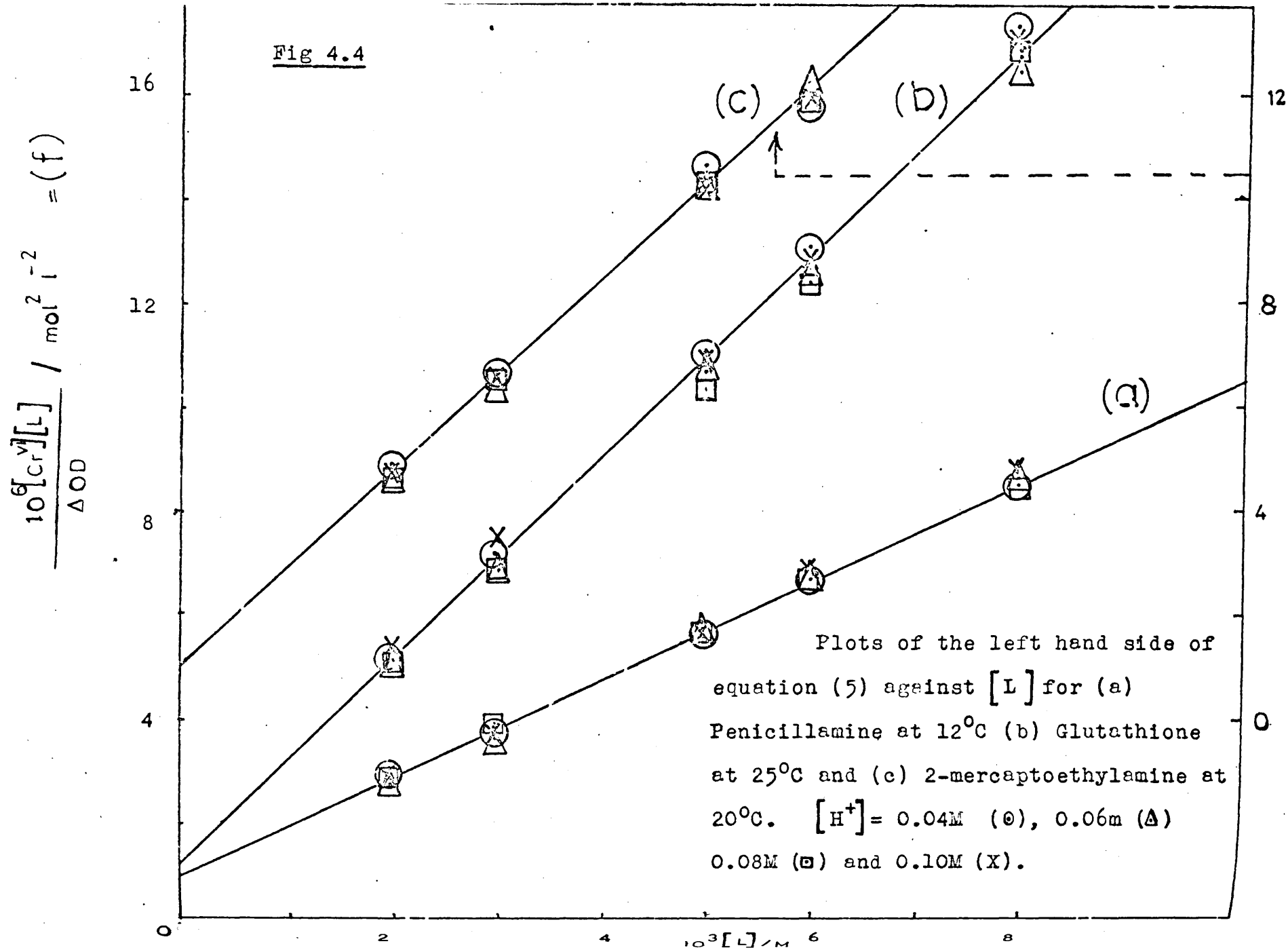
Under the conditions where uncomplexed Chromium(VI) was present at equilibrium, the measured value of OD_{eqm} was found to be independent of $[H^+]_o$. Applying the general assumption that $HCrO_4^-$ only forms a 1:1 complex under the conditions employed in these studies equation (5) may be derived.

$$\frac{[Cr^{VI}]\,[L]}{\Delta OD} = \frac{[L]}{\Delta\varepsilon . l} + \frac{1}{K . \Delta\varepsilon . l} \qquad (5)$$

Plots of $\frac{[Cr^{VI}]_t [L]}{\Delta OD}$ against $[L]$ gave good linearity at all the temperatures studied (see Fig 4.4). The absence of any variation of intercept with differing hydrogen ion concentrations is an indication that little or no net uptake or loss of protons is involved in the complex formation. In addition, the linearity of the above plot suggests that the assumption of a solely mono complex formation is justified.

Deranleau[160] has observed that when the concentration of the complex formed in such reactions is not negligible as compared to the concentration of the reagent in excess, the equilibrium constants obtained from such plots are always less than the true value. If equation

Fig 4.4



Plots of the left hand side of equation (5) against $[L]$ for (a) Penicillamine at 12°C (b) Glutathione at 25°C and (c) 2-mercaptoethylamine at 20°C. $[H^+]$ = 0.04M (⊙), 0.06m (Δ) 0.08M (⊡) and 0.10M (X).

TABLE 4.2

Thermodynamic parameters for Complex formation derived using equation (5) designated (a) and also those derived from variation in the value of $\Delta\varepsilon$ designated (b) ref 160 .

L = Penicillamine

$T^{o}C$	12.0	17.0	25.0	30.0
$K^{(a)}_{1mol^{-1}}$	1010±20	886±15	680±30	475±25
$\varepsilon^{(a)}_{1mol^{-1}cm^{-1}}$	1270±30	1254±40	1230±50	1280±20
$K^{(b)}_{1mol^{-1}}$	1150±50	889±40	700±40	510±30
$\varepsilon^{(b)}_{1mol^{-1}cm^{-1}}$	1248	1248	1228	1268

ΔG = -3.85±0.4 KCal mol^{-1}; ΔH = -6.8±0.6 Kcal mol^{-1}

ΔS = -9.9±3 cal $K^{-1}mol^{-1}$

L = Glutathione

$T^{o}C$	15.0	20.0	25.0	30.0
$K^{(a)}_{1mol^{-1}}$	1568±100	1320±60	1263±40	1064±40
$\varepsilon^{(a)}_{1mol^{-1}cm^{-1}}$	1387±40	1309±20	1284±10	1348±30
$K^{(b)}_{1mol^{-1}}$	1643±100	1550±100	1436±50	1180±80
$\varepsilon^{(b)}_{1mol^{-1}cm^{-1}}$	1388	1288	1288	1367

ΔG = 4.2±0.5 Kcal mol^{-1}; ΔH = 4.5±0.5 Kcal mol^{-1}

ΔS = -1.1±1 cal $K^{-1}mol^{-1}$

L = β-mercaptoethylamine

$T^{o}C$	20.0	25.0	30.0
$K^{(a)}{}_{1mol^{-1}}$	1394±100	1200±80	1152±60
$\varepsilon^{(a)}{}_{1mol^{-1}cm^{-1}}$	1331±30	1339±40	1313±30
$K^{(b)}{}_{1mol^{-1}}$	1470±100	1300±100	1170±100
$\varepsilon^{(b)}{}_{1mol^{-1}cm^{-1}}$	1328	1328	1308

ΔG = -4.2±0.4 Kcal mol^{-1}; ΔH = -3.7±1 K cal mol^{-1}

ΔS = 1.8±1 cal $K^{-1}mol^{-1}$

complex would be expected in these studies. If O,S bonding configuration were present within the chromium(VI) species, then β-mercaptoethylamine which has no carboxylic group is expected to behave fairly differently towards chromium (VI). Not only does the spectrum of the intermediate species formed by this ligand exhibit a λ_{max} at the same region as that formed by glutathione but also the K value obtained is almost twice as large as that of penicillamine. The fact that this complex is the most stable of all the three would also argue against an O,S bonding chelate complex. It might be tempting to postulate an N,S bonding configuration for the complex species. However, since the reactants are presumed to be in the zwitterion form with the amino groups protonated, no bond is expected between N of this group and chromium (VI).

A less substantial piece of evidence against chelation is provided by the low value of the entropy of complex formation (see Table 4.2).

Cysteine which is structurally related to these ligands form similar chromate (VI) ester[134] with an equilibrium constant of 1030 l mol^{-1} and a λ_{max} occuring at 420nm. The value of 1410 l $mol^{-1}cm^{-1}$ for the extinction coefficient is also similar to those obtained in these studies.

From all these observations, equilibria (7) and (8) may be postulated for the formation of the intermediate

complex.

$$HCrO_4^- + H_2L \overset{k_1}{\rightleftharpoons} HLCrO_3^- + H_2O \qquad (7)$$

$$HCrO_4^- + H_3L^+ \overset{k_2}{\rightleftharpoons} H_2LCrO_3 + H_2O \qquad (8)$$

Since the measured values of K and $\Delta\varepsilon$ in all these reactions are independent of acid concentration, equation (9) and (10) can be postulated to hold within experimental errors.

$$\Delta\varepsilon_{HLCrO_3^-} = \Delta\varepsilon_{H_2LCrO_3} \qquad (9)$$

$$K_1 = K_2 \qquad (10)$$

The above results indicate that it is impossible to differentiate between the overall complex formation reactions involving the two species of the ligand, H_2L and H_3L^+. It may also be viewed as confirming the experimental evidence from pH measurements that only a neglible amount of the latter species is formed under the experimental conditions used.

2. Formation Kinetics

All the kinetic measurements were carried out using excess of the ligands. Plots of $\log(OD_\infty - OD_t)$ against time gave good linearity for over 80% of the reaction

and the pseudo-first-order rate constants k_{obs} were evaluated from the slopes of these plots (see Fig 4.5). These are tabulated in Table 4.3.

Plots of k_{obs} as a function of $[\text{ligand}]_o$ at constant $[H^+]_o$ were linear with positive intercepts (see Fig 4.6 - 4.8). This is considered as evidence of the validity of the argument as to the nature of the reacting ligand species in the overall equilibrium reaction.

Representing the total ligand concentration in each case as H_2L, the various reactions contributing to complex formation can be formulated as in equations (11) and (12)

$$HCrO_4^- + H_2L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HLCrO_3 + H_2O \qquad (11)$$

$$HCrO_4^- + H_2L + H^+ \underset{k_b^{H^+}}{\overset{k_f^{H^+}}{\rightleftharpoons}} HLCrO_3 + H_2O + H^+ \qquad (12)$$

On the basis of this scheme equation (13) can readily be derived

$$k_{obs} = \left(k_f^{H^+} [L]_o + k_b^{H^+}\right) [H^+]_o + k_f [L]_o + k_b \qquad (13)$$

Rearrangement of equation (13) yields equation (14)

$$k_{obs} = \left(k_f + k_f^{H^+} [H^+]_o\right) [L]_o + k_b + k_b^{H^+} [H^+]_o \qquad (14)$$

TABLE 4.3

Rate constants for the formation of the Cr(VI) - L complex.

$[Cr(VI)] = 2 \times 10^{-4}M$; $I = 1.0M$

L = Penicillamine $\lambda = 420nm$

Temp. 12°C

$[H^+] = 0.04M$

$[L]10^3/M$	$10^2k_{obs}/S^{-1}$
2.0	0.464
3.0	0.605
5.0	0.87
6.0	1.04
8.0	1.38

$[H^+] = 0.06M$

$[L]10^3/M$	$10^2k_{obs}/S^{-1}$
2.0	0.601
3.0	0.86
5.0	1.23
6.0	1.39
8.0	1.83

$[H^+] = 0.08M$

$[L]10^3/M$	$10^2k_{obs}/S^{-1}$
2.0	0.755
3.0	1.08
5.0	1.41
6.0	1.64
8.0	2.07

$[H^+] = 0.10M$

$[L]10^3/M$	$10^2k_{obs}/S^{-1}$
2.0	0.867
3.0	1.12
5.0	1.65
6.0	2.00
8.0	2.45

Temp 17°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^2 k_{obs}/s^{-1}$
2.0	0.739
3.0	0.936
5.0	1.357
6.0	1.614
8.0	2.052

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^2 k_{obs}/s^{-1}$
2.0	0.948
3.0	1.202
5.0	1.741
6.0	1.906
8.0	2.495

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	$10^2 k_{obs}/s^{-1}$
2.0	1.17
3.0	1.49
5.0	2.04
6.0	2.41
8.0	3.109

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	$10^2 k_{obs}/s^{-1}$
2.0	1.301
3.0	1.77
5.0	2.486
6.0	2.90
8.0	3.71

Temp 25°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	0.790
3.0	1.027
5.0	1.538
6.0	1.796
8.0	2.22

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	1.26
3.0	1.589
5.0	2.21
6.0	2.565
8.0	3.429

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	1.76
3.0	2.129
5.0	2.695
6.0	3.425
8.0	4.458

$[H^+]$ = 0.08M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	2.21
3.0	2.63
5.0	3.64
6.0	3.90
8.0	4.88

Temp 30°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	1.79
3.0	2.30
5.0	3.21
6.0	3.78
8.0	4.23

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	2.34
3.0	2.83
5.0	3.76
6.0	4.14
8.0	5.13

$[H^+]_o$ = 0.08M

$[L]10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	2.96
3.0	3.53
5.0	4.54
6.0	5.34
8.0	6.545

$[H^+]$ = 0.10M

$[L]_o 10^3$/M	$10^2 k_{obs}/S^{-1}$
2.0	3.517
3.0	3.992
5.0	5.514
6.0	6.084
8.0	7.75

L = Glutathione λ = 430nm

Temp 15°C

$[H^+]$ = 0.04M

$[L]_0 10^3/M$	k_{obs}/S^{-1}
2.0	0.056
3.0	0.072
5.0	0.106
6.0	0.126
8.0	0.146

$[H^+]$ = 0.06M

$[L]_0 10^3/M$	k_{obs}/S^{-1}
2.0	0.080
3.0	0.108
5.0	0.154
6.0	0.186
8.0	0.240

$[H^+]$= 0.08M

$[L]_0 10^3/M$	k_{obs}/S^{-1}
2.0	0.1120
3.0	0.147
5.0	0.216
6.0	0.258
8.0	0.320

$[H^+]$ = 0.10M

$[L]_0 10^3/M$	k_{obs}/S^{-1}
2.0	0.123
3.0	0.184
5.0	0.272
6.0	0.320
8.0	0.410

Temp = 20°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.0336
3.0	0.0464
5.0	0.066
6.0	0.076
8.0	0.092

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.070
3.0	0.093
5.0	0.136
6.0	0.154
8.0	0.200

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.108
3.0	0.139
5.0	0.202
6.0	0.232
8.0	0.300

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.134
3.0	0.182
5.0	0.268
6.0	0.310
8.0	0.396

Temp. 25°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.0472
3.0	0.062
5.0	0.089
6.0	0.101
8.0	0.127

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.093
3.0	0.123
5.0	0.184
6.0	0.208
8.0	0.264

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.1430
3.0	0.186
5.0	0.256
6.0	0.310
8.0	0.392

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.192
3.0	0.254
5.0	0.366
6.0	0.424
8.0	0.550

Temp = 30°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.122
3.0	0.164
5.0	0.232
6.0	0.262
8.0	0.338

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.188
3.0	0.240
5.0	0.344
6.0	0.396
8.0	0.510

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.258
3.0	0.356
5.0	0.500
6.0	0.575
8.0	0.730

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.324
3.0	0.424
5.0	0.616
6.0	0.730
8.0	0.935

L = β - mercaptoethylamine

Temp 20°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.0395
3.0	0.0524
5.0	0.080
6.0	0.093
8.0	0.120

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.0604
3.0	0.077
5.0	0.117
6.0	0.144
8.0	0.178

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.077
3.0	0.104
5.0	0.159
6.0	0.180
8.0	0.244

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.098
3.0	0.132
5.0	0.198
6.0	0.234
8.0	0.288

Temp 25°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.025
3.0	0.0336
5.0	0.0536
6.0	0.062
8.0	0.076

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.0512
3.0	0.068
5.0	0.105
6.0	0.120
8.0	0.152

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.070
3.0	0.097
5.0	0.150
6.0	0.170
8.0	0.220

$[H^+]_o$ = 0.08M

$[L]_o 10^3$	k_{obs}/S^{-1}
2.0	0.094
3.0	0.126
5.0	0.192
6.0	0.224
8.0	0.288

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.124
3.0	0.164
5.0	0.246
6.0	0.282
8.0	0.360

Temp 30°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.069
3.0	0.095
5.0	0.136
6.0	0.154
8.0	0.194

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.102
3.0	0.134
5.0	0.198
6.0	0.230
8.0	0.292

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.138
3.0	0.175
5.0	0.256
6.0	0.306
8.0	0.380

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	k_{obs}/S^{-1}
2.0	0.172
3.0	0.216
5.0	0.324
6.0	0.380
8.0	0.488

$$= \alpha [L]_o + \beta$$

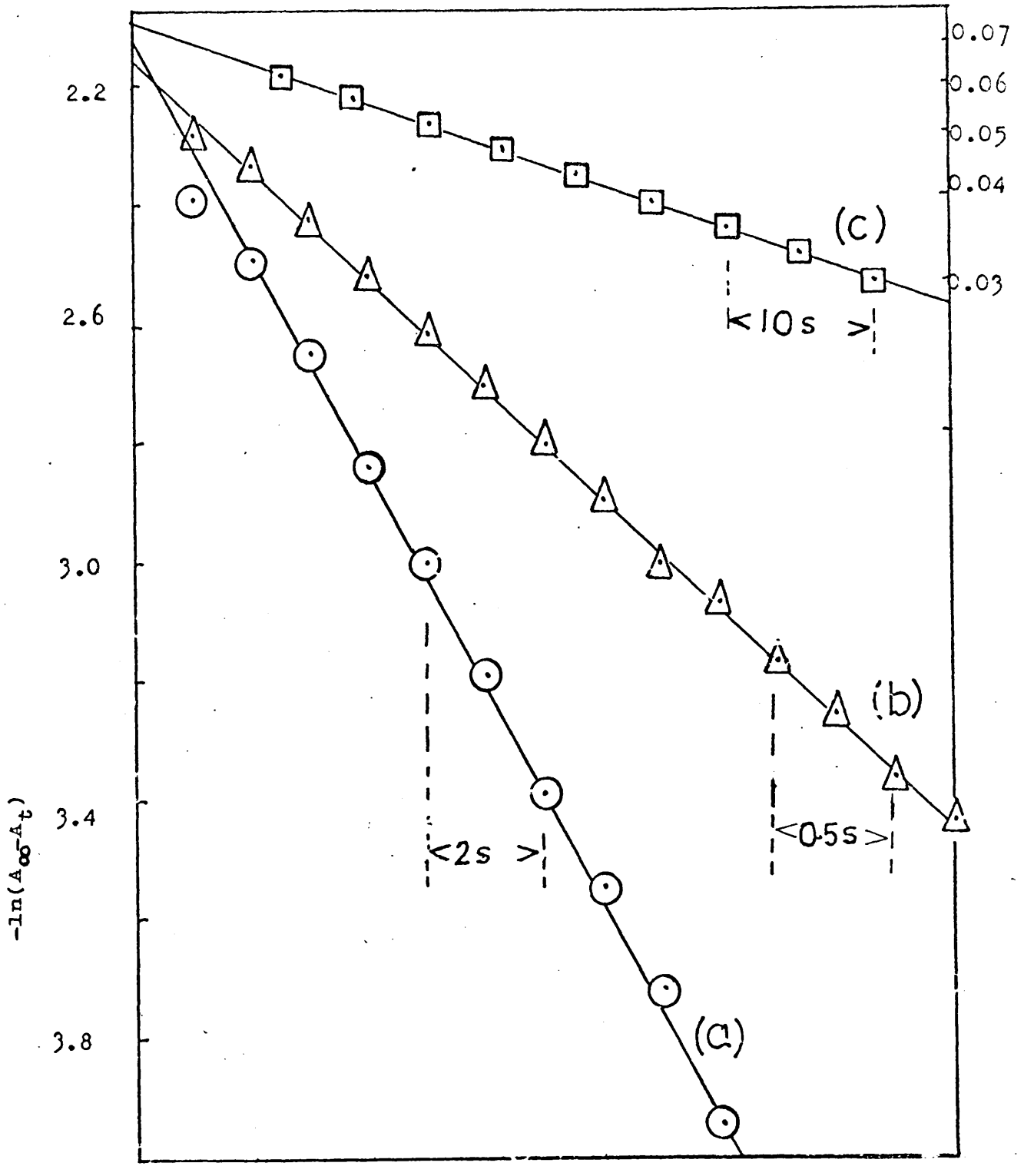
The kinetic data agrees well with the scheme where the plot of kobs against $[L]_o$ gave good linearity (fig 4.6 - 4.8) at constant $[H^+]_o$. On plotting the slope (α) and intercept β obtained from such plots against $[H^+]_o$ good straight lines were obtained in all the cases (see Fig 4.9 and 4.10). The various rate constants, $k_f^{H^+}$, k_f and $k_b^{H^+}$ were derived from the slope and intercept of such plots. The values of these constants obtained for all the ligands at various temperatures are presented in Table 4.4 . In most of the reactions the value of k_b was found to be very small and could not be evaluated accurately.

The Hydrogen - Ion - Dependent Pathway

The $k_f^{H^+}$ values in Table 4.4 which also include the equivalent kinetic parameter for the structurally related cysteine, are in each case less than 10^3 l^2 mol^{-2} S^{-1}. Comparison of these values with those so far obtained for such reactions ($(1 - 7) \times 10^5$ $l^2 mol^{-2} S^{-1}$) shown in Table 2.3 (chapter II), indicate that the rate constants in the present studies are significantly lower.

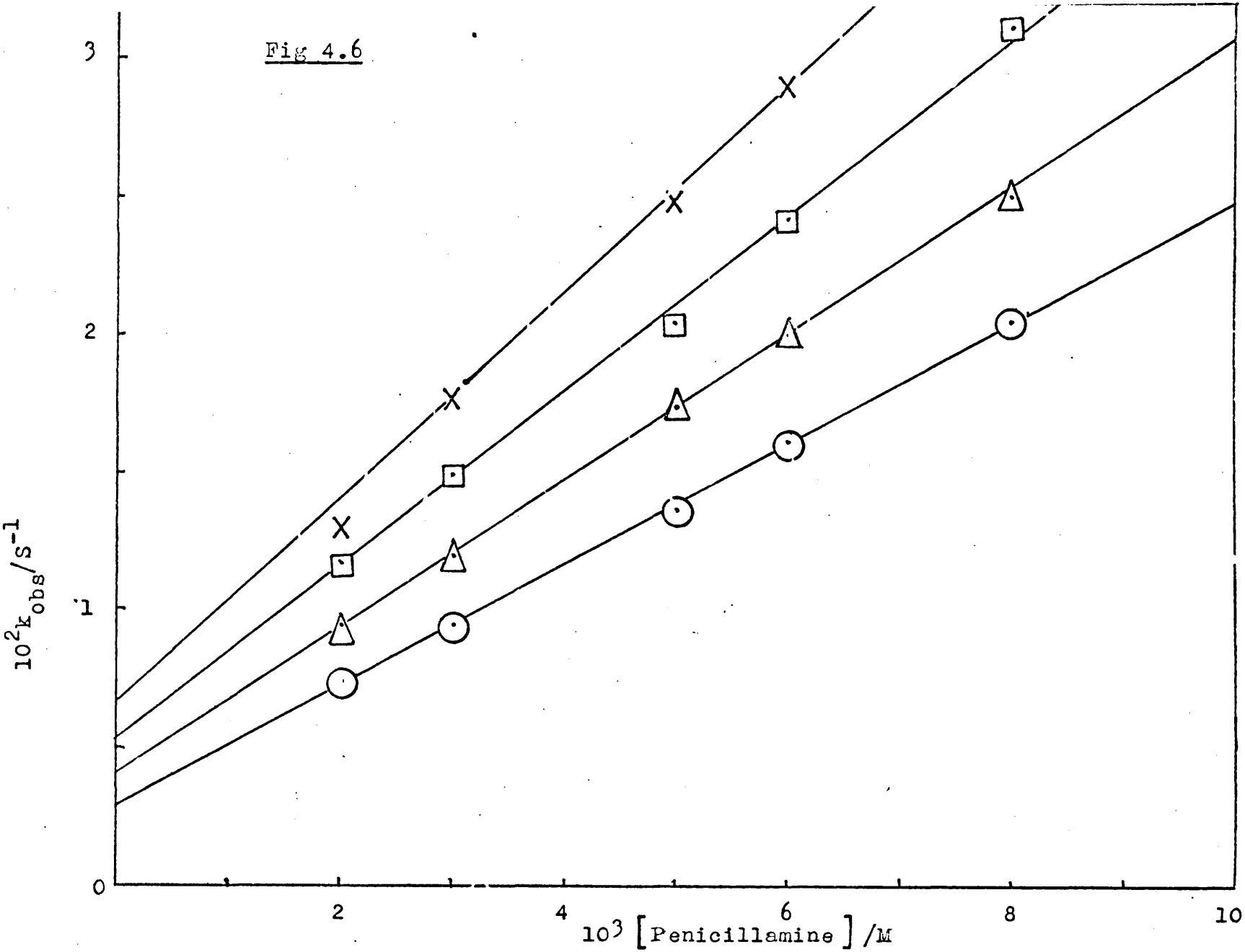
Two mechanisms have been postulated to account for the observed kinetic data and have been discussed earlier. One approach proposed by Haight[112], Beattie[104] and their co-workers postulated the formation of a weak complex

Fig 4.5

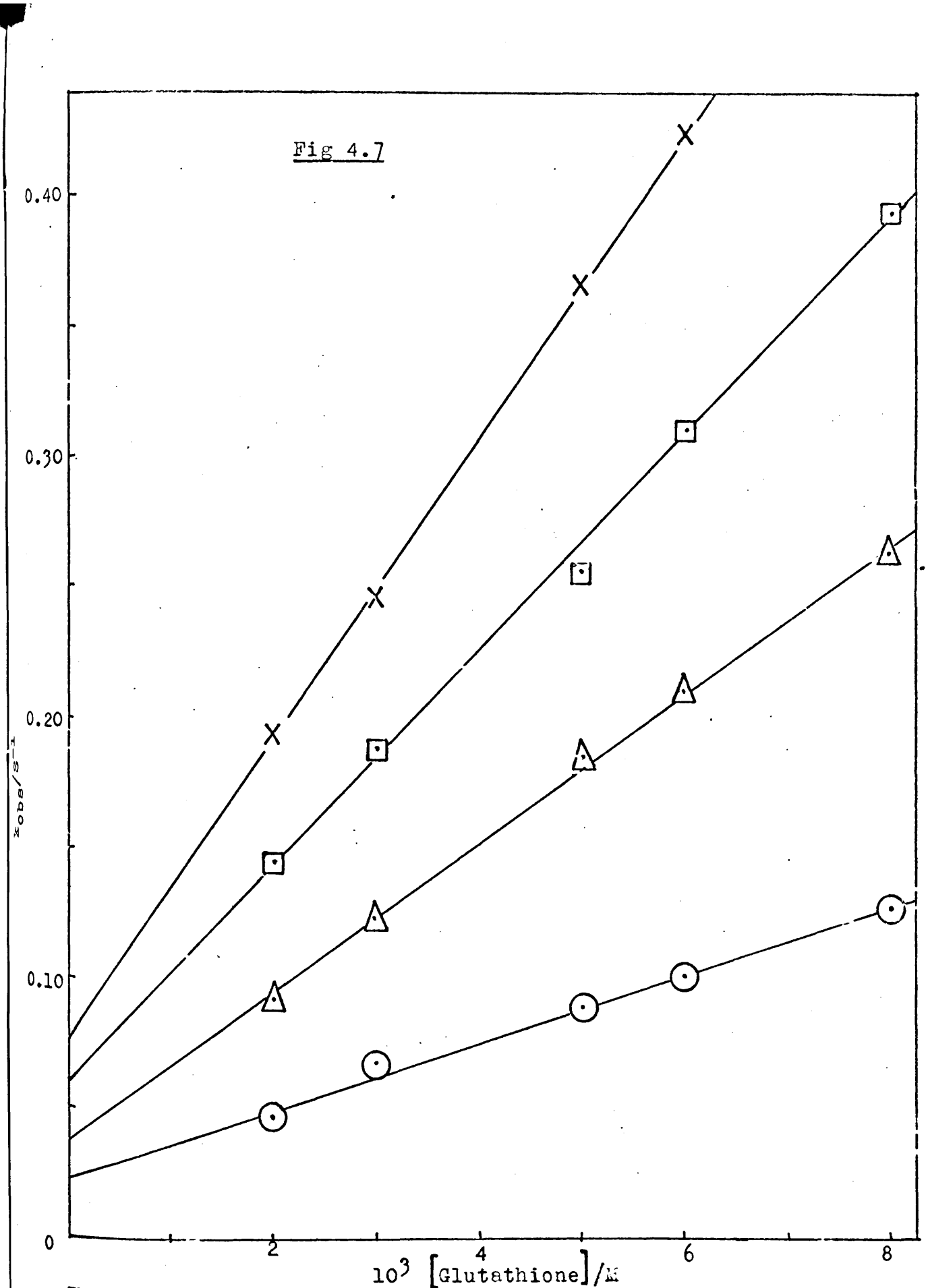


Pseudo-first-order plots for the formation of chromate esters with (a), [Glutathione] 5×10^{-3}M, $[H^+] = 0.04$M, I = 1.0M T = 25°C; (b), [2-Mercaptoethylamine] 8×10^{-3}M, $[H^+] = 0.10$M I = 1.0M T = 25° and (c), [Penicillamine] 2×10^{-3}M, $[H^+] = 0.06$M, I = 1.0M, T = 30.0°C. $[Cr^{VI}] = 2 \times 10^{4}$M

Fig 4.6

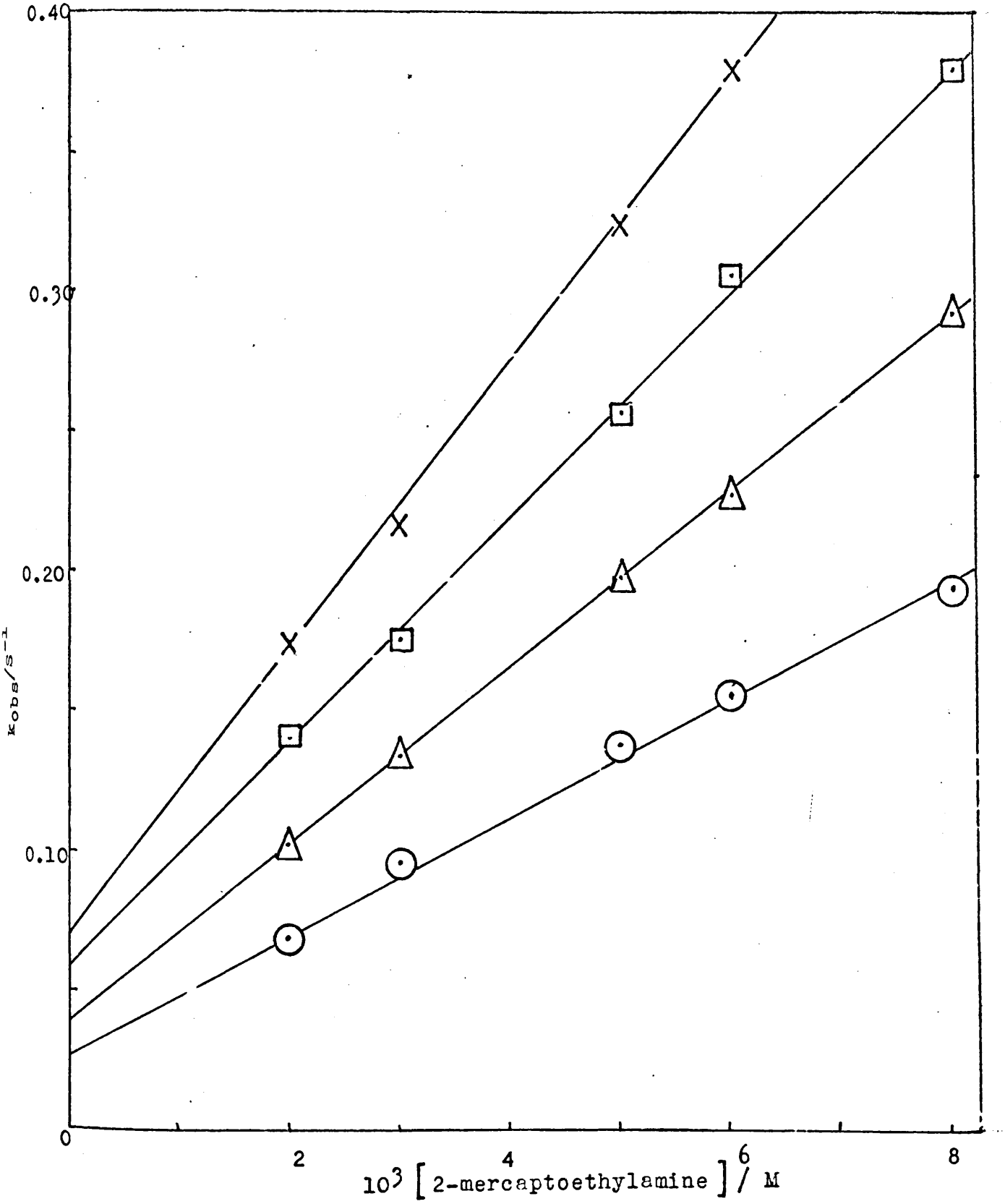


The dependence of k_{obs} on initial Penicillamine concentration for the chromate (VI) ester formation at 17°C. $[H^+]$ = 0.04M (⊙), 0.06M (△), 0.08M (⊡) and 0.10M (X).

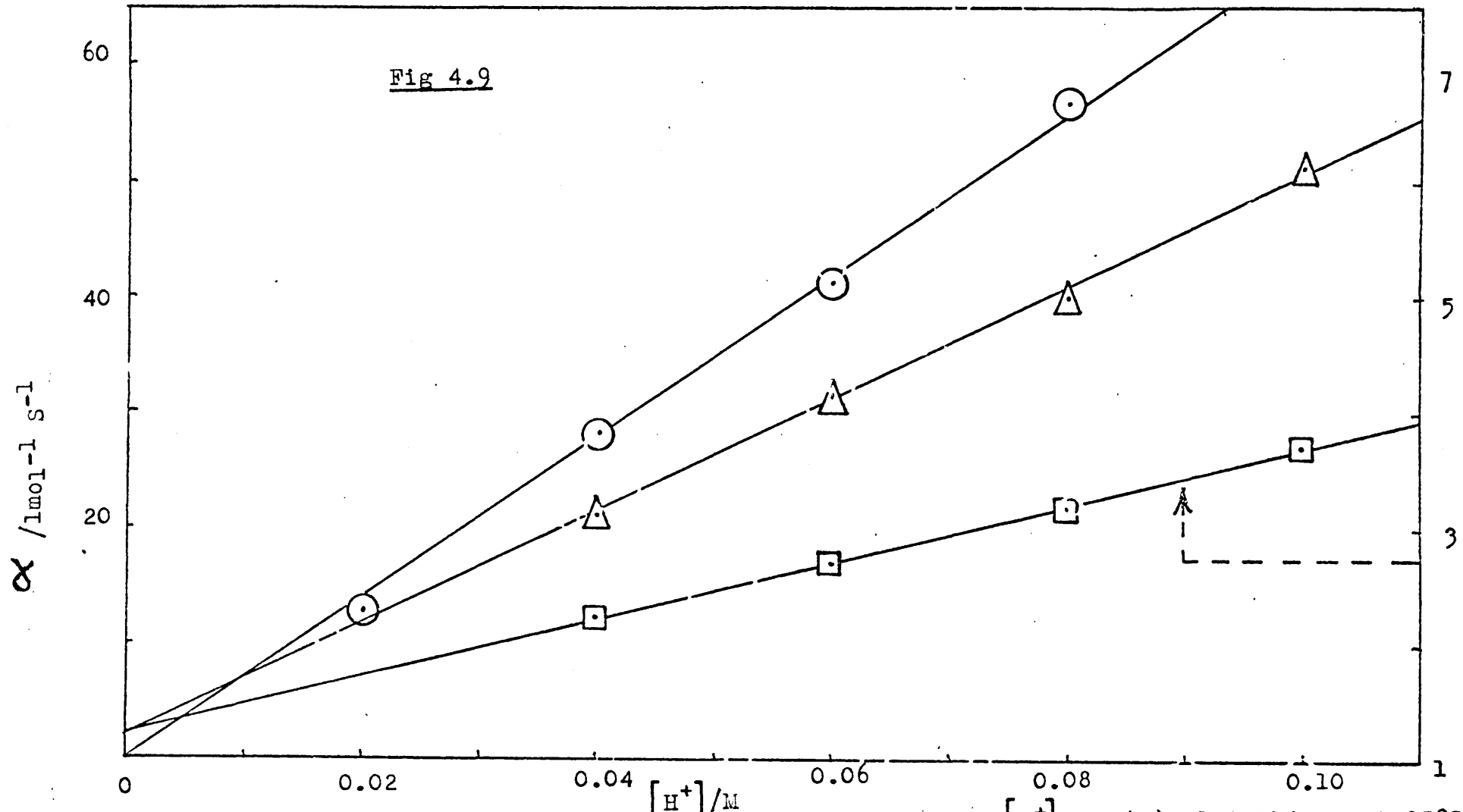


The dependence of k_{obs} on initial glutathione concentration for the chromate (VI) ester formation at 25°C. $[H^+]$ = 0.02M (⊙), 0.04M (△), 0.06M (⊡) and 0.08M (X).

Fig 4.8

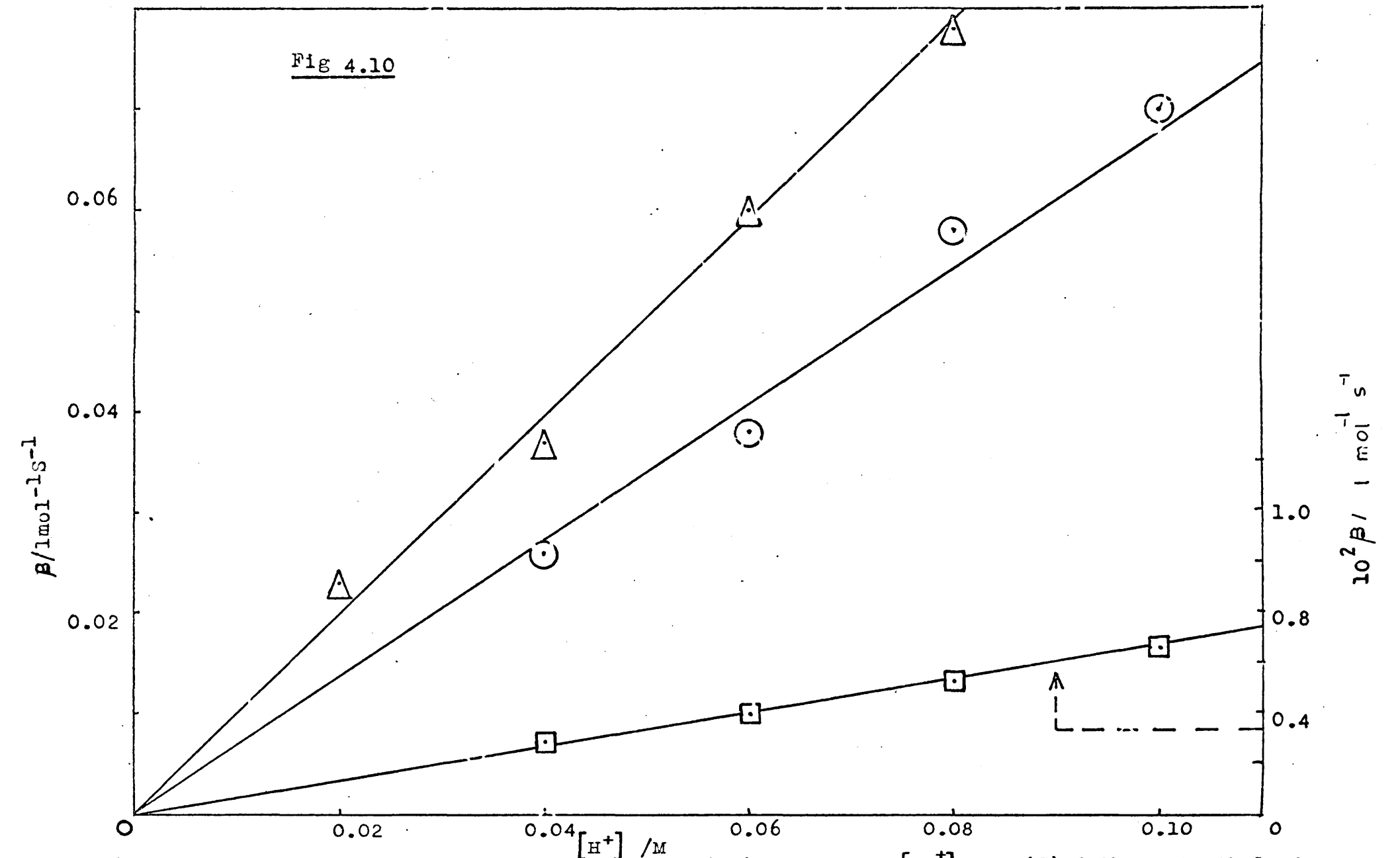


The dependence of k_{obs} on initial mercaptoethylamine concentration for the chromate (VI) ester formation at 30°C. $[H^+]$ = 0.04M (⊙) 0.06M (△), 0.08M (⊡) and 0.10M (X).



Dependence of α (slope) from equation (14) on the initial $[H^+]$ for (⊙) glutathione at 25°C (△) 2-mercaptoethylamine at 30°C and (⊡) Penicillamine at 17°C.

Fig 4.10



Dependence of β (intercept) from equation (14) on initial $[H^+]$ for (⊙) 2-Mercaptoethylamine at 30°C, (Δ) glutathione at 25°C and (⊡) Penicillamine at 17°C.

TABLE 4.4

Rate constants for the formation of the intermediate complex species between chromium (VI) and the various thiols (L) at different temperatures.

L = Penicillamine

T°C	$10^{-2}k_f^{H+}/l^2mol^{-2}S^{-1}$	k_f l mol^{-1} S^{-1}	k_b^{H+}/l $mol^{-1}S^{-1}$
12.0	0.188±0.005	0.75±0.4	0.037±0.02
17.0	0.25±0.01	1.20±0.7	0.066±0.03
25.0	0.338±0.02	1.82±2.0	0.160±0.10
30.0	0.463±0.06	2.10±1.0	0.219±0.15

ΔH^*/Kcal mol^{-1} 5.9±2

ΔS^*/cal $K^{-1}mol^{-1}$ -31.8±12

L = Glutathione

T°C	$10^{-2}k_f^{H+}/l^2mol^{-2}S^{-1}$	k_f/l mol^{-1} S^{-1}	k_b^{H+}/l $mol^{-1}S^{-1}$
15.0	4.40±0.10	-	0.36±0.15
20.0	5.33±0.20	-	0.68±0.40
25.0	7.06±0.50	-	0.98±0.60
30.0	9.60±0.50	-	1.29±0.80

ΔH^*/Kcal mol^{-1} 10.2±4

ΔS^*/ cal $K^{-1}mol^{-1}$ - 11.4±3

L = β-Mercaptoethylamine

T°C	$10^{-2}k_f^{H^+}$ / $l^2 mol^{-2} s^{-1}$	k_f / $l\ mol^{-1} s^{-1}$	$k_b^{H^+}$ / $l\ mol^{-1} s^{-1}$
20.0	3.22±0.10	0.50±0.30	0.32±0.10
25.0	3.79±0.15	1.70±0.60	0.44±0.20
30.0	4.88±0.20	2.0±1.0	0.68±0.35

ΔH^* / Kcal mol^{-1} 7.2±3

ΔS^* / cal $K^{-1} mol^{-1}$ -24.7±10

L = cysteine[a]

T°C	$10^{-2}k_f^{H^+}$ / $l^2 mol^{-2} s^{-1}$	k_f / $l\ mol^{-1} s^{-1}$
25	1.30±0.20	2±1

ΔH^* / Kcal mol^{-1} 7±3

ΔS^* / cal $K^{-1} mol^{-1}$ -24.0±11

(a) J.P. McCann and A. McAuley, J. Chem. Soc. Dalton, 1975, 783.

followed by rate - determining diffusion controlled protonation of the OH^- group of $HCrO_4^-$ with the subsequent loss of the water molecule. An alternative mechanism was put forward by Haim[111] who argued that the reaction is likely to involve protonation of the OH^- group attached to $HCrO_4^-$ as the first step followed by rate determining water loss from the penta co-ordinate complex formed.

The third possibility that could be considered assuming the release of the proton and water molecule occur faster, is that the formation of the first intermediate is infact the rate determining step. This however, would not give rise to the observed dependence of the rate on hydrogen ion concentration. It is obvious therefore that protonation must occur before the rate - determining step. This would seem to give added weight to Haim's mechanism but assuming this holds, water loss would be expected to take place with a specific rate probably greater than 10^5 S^{-1}, as the equilibrium constant for the formation of H_2CrO_4 is almost certainly less than unity (see Table 2.1 chapter II). The $k_f^{H^+}$ values obtained in these studies are in the range $(0.3 - 7) \times 10^2$ $l^2mol^{-2}S^{-1}$ which is $\sim 10^3$ times smaller than those obtained for all other similar reactions previously studied. It seems reasonable to conclude therefore that in the present studies either formation

of the Cr - S bond or dissociation of the S - H bond is rate - determining.

An estimate can be made of the rate of proton-transfer from the S-H bond from the known dissociation constant K_a^1, if it is assumed that the strength of the S-H bond is unaffected by a weak S----Cr linkage. Since the rate of recombination of the proton with its conjugate base is probably diffusion-controlled[45,145] the rate of proton dissociation can be estimated as,

$$RSH \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} RS^- + H^+ \qquad (15)$$

$$K_a^1 = \frac{k_d}{k_{-d}} \qquad (16)$$

$$k_d \simeq 10^{10} K_a^1 \qquad (17)$$

Values of k_d obtained in this way are less than 10^2 S^{-1} since the pK_a^1 values corresponding to the loss of proton from the - SH group is > 8 in all the ligands investigated.

It is therefore quite tempting to postulate deprotonation as the rate - determining step with water loss being the fast final step. If this were the case and the principle of microscopic reversibility assumed, the rate of aquation of the complex would be expected to be controlled by protonation which is usually

diffusion controlled. Such a situation is unlikely not only because it is unusual for a rate-determining step to be diffusion - controlled but also because the rate - constant for acid - catalysed aquation of the complex would be expected to be $\sim 10^{10}$ l mol^{-1} S^{-1} as opposed to the observed value of < 2 (Table 4.4).

From all the considerations above a conclusion can be drawn that the rate - determining step is the formation of the Cr - S bond. Investigation of a system involving similar ligand structure but with the proton in the -SH group being replaced by a bulky group like the methyl group might throw some light on the mechanism involved in these reactions.

The Hydrogen - Ion Independent Pathway

The mechanism previously proposed[104] for this pathway involves proton-transfer to form the departing water molecule (equation 18).

$$\begin{array}{l} X \text{ -------} CrO_3^- \\ | \qquad\quad | \\ H \qquad OH \end{array} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{l} X - CrO_3^- \\ | \\ H_2O \end{array} \qquad (18)$$

The observed proportionality of k_f to the acid strength of the substrate has led to the proposal that the loss of proton from the loosely co-ordinated acidic substrate is likely to be the rate determining step.

The values of k_1 for all the ligands studied can be estimated if it is assumed that this is equivalent to k_d the proton dissociation rate constant of non-bonded HX using equation (17). Using the value of $K_o \sim 10^{-5}$ 1 mol^{-1} estimated for similar reactions[104,112] k_f can be calculated from equations (17) and (19).

$$k_f = K_o k_d \qquad (19)$$

The values of k_f obtained from such calculations using maximum possible values of K_o and K_a^1 are two orders of magnitude less than that obtained experimentally in these studies (see Table 4.4). It is interesting to note that the experimental values compared well with that measured for the corresponding process with L - cysteine[134].

II The Electron-Transfer Reactions

(a) Stoicheiometry and Final Products

The ligand : Chromium (VI) ratios using acidimetric titration method[142] were found to be 3.0±0.1 in the reactions involving Penicillamine and glutathione suggesting an overall reaction given by equation (20).

$$nH^+ + 2HCrO_4^- + 6L \longrightarrow 2Cr(III) + 3L^1 - L^1 \qquad (20)$$

Using this method described in detail in chapter I and

the experimental conditions referred to earlier in this chapter, two complexes were observed on the columns in both cases.

The first species isolated from the ion exchange column containing the products from penicillamine reaction with Cr(VI) is purple in colour. A comparison of the elution rate using $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$ as references and also appropriate solvent mixtures outlined in chapter I show this species to be doubly charged and contained about 60% of the total chromium. The second species on the column has a more intense purple colour and could not be eluted as a band even with an eluent containing 2M $HClO_4$ and 4M $NaClO_4$. However, the complex appeared to aquate on prolonged elution to yield $Cr(H_2O)_6^{3+}$ which could be eluted with the solvent mixture as above. This latter complex which contains $\lesssim$ 40% of the total chromium is presumed to be a dimeric 4+ charged species. This could have resulted from a parallel reaction of $Cr_2O_7^{2-}$ a fact which contrasts with currently held views about the reactivity of this species as compared to $HCrO_4^-$.

It is interesting to point out that similar results were obtained in the chromium (VI) oxidation of L-cysteine.

Two complex species were also identified and isolated in the product mixtures from glutathione reactions with chromium (VI). Using the analytical methods

referred to previously, the first bluish-purple species isolated was presumed to be the aquo species with a +3 charge. Confirmation of this was obtained from the spectrum of the species which was identical to that of $Cr(H_2O)_6^{3+}$ and also the fact that no SO_4^{2-} precipitation was observed when sulphur analysis was carried out as outlined in chapter I. The second species which was greenish in colour also carries a +3 charge and contained ~40% of the total chromium. About 50% of the first species was formed while the remaining 10% was the dimeric +4 species which was difficult to isolate. Although the presence of sulphur in the greenish complex was confirmed by $BaSO_4$ precipitation, inconsistent Cr : S ratios were obtained possibly as a result of the low concentration of sulphur being determined.

Products identical to those obtained for glutathione were identified in the mercaptoethylamine reaction with chromium. The only difference is that 78% of the aquo species and 20% of the green species were formed in the latter case with no trace of the dimeric species.

From all the observations above including the stoicheiometric results, it seems inevitable to conclude that the purple species in the penicillamine reaction and the two green species in the reactions involving the other two ligands must contain the disulphide co-ordinated to the chromium probably through either O and N bonding.

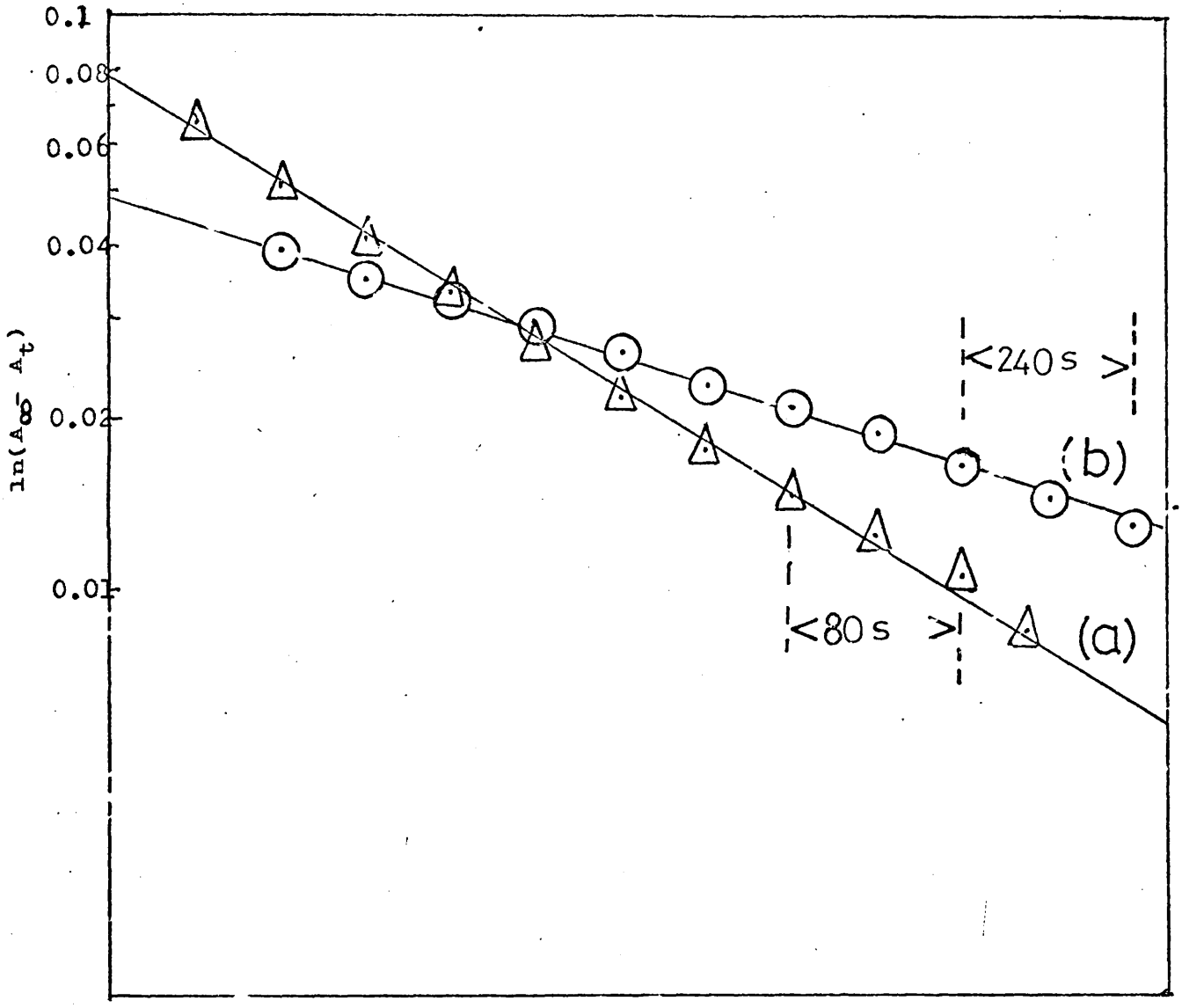
Clearly a method capable of quantitatively determining the amount of sulphur present in low concentrations such as those under consideration is necessary to establish beyond reasonable doubt the nature of these species.

(b) Kinetics of the Electron-Transfer Reactions

The electron-transfer reactions of both penicillamine and glutathione were studied. Under the experimental conditions used the redox reaction involving mercapto-ethylamine was found to be very slow.

The redox reactions of the two systems were investigated over a temperature range of 12-30°C using identical conditions as those used in the study of the formation reactions although the ligand concentration range in the glutathione case was extended to 15×10^{-3}M. Under these conditions the redox reactions are at least a factor of ten slower than the formation reactions. Pseudo-first order rate constants were evaluated from plots of In $(OD_t - OD_\infty)$ as a function of time (Fig 4.11) and the values obtained are shown in Table 4.5. On plotting k_{obs} as a function of the ligand no direct first or second-order dependence was observed except in the glutathione reactions where a high equilibrium constant had been evaluated (see Table 4.2). Since the complex formed is a kinetically important species and since at lower ligand concentrations appreciable amounts of Cr(VI) would be expected to remain uncomplexed

Fig 4.11



Pseudo-first-order plots for the decay of chromate esters involving (a) [glutathione] 8 x10^{-3}M, [H^+]= 0.10M, T = 30°C and (b) [Penicillamine] 2 x 10^{-3}M, [H^+]= 0.06M, T = 12°C, I = 1.0M.

TABLE 4.5

Rate Constants for the Redox Reactions

$[Cr(VI)]_o = 2 \times 10^{-4}M$; I = 1.0M

L = Penicillamine λ = 420nm

Temp 12°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3/M$	$10^3 k_{obs}/s^{-1}$
2.0	0.590
3.0	0.758
5.0	0.991
6.0	1.09
8.0	1.23

$[H^+]_o$ = 0.06M

$[L]_o 10^3/M$	$10^3 k_{obs}/s^{-1}$
2.0	0.89
3.0	1.10
5.0	1.35
6.0	1.43
8.0	1.604

$[H^+]_o$ = 0.08M

$[L]_o 10^3$	$10^3 k_{obs}/s^{-1}$
2.0	1.14
3.0	1.36
5.0	1.67
6.0	1.78
8.0	1.94

$[H^+]_o$ = 0.10M

$[L]_o 10^3$	$10^3 k_{obs}/s^{-1}$
2.0	1.46
3.0	1.66
5.0	1.96
6.0	2.11
8.0	2.32

Temp 17°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
2.0	0.959
3.0	1.164
5.0	1.529
6.0	1.666
8.0	1.838

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
2.0	0.948
3.0	1.658
5.0	1.912
6.0	2.059
8.0	2.361

$[H^+]_o$ = 0.08M

$[L]_o 10^3$	$10^3 k_{obs}/s^{-1}$
2.0	1.572
3.0	2.03
5.0	2.45
6.0	2.588
8.0	2.907

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
2.0	1.99
3.0	2.499
5.0	3.033
6.0	3.109
8.0	3.409

Temp 25°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
2.0	0.853
3.0	1.014
5.0	1.420
6.0	1.599
8.0	2.044

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
2.0	1.55
3.0	1.902
5.0	2.476
6.0	2.624
8.0	3.014

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
2.0	2.20
3.0	2.753
5.0	3.508
6.0	3.628
8.0	3.837

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
2.0	2.67
3.0	3.37
5.0	4.36
6.0	4.73
8.0	5.02

Temp $30^{o}C$

$[H^{+}]_{o}$ = 0.04M

$[L]_{o}10^{3}/M$	$10^{3}k_{obs}/s^{-1}$
2.0	2.14
3.0	2.74
5.0	3.46
6.0	3.74
8.0	4.08

$[H^{+}]_{o}$ = 0.06M

$[L]_{o}10^{3}/M$	$10^{3}k_{obs}/s^{-1}$
2.0	3.22
3.0	3.98
5.0	5.32
6.0	5.366
8.0	5.51

$[H^{+}]_{o}$ = 0.08M

$[L]_{o}10^{3}/M$	$10^{3}k_{obs}/s^{-1}$
2.0	4.173
3.0	5.21
5.0	6.547
6.0	6.71
8.0	7.36

$[H^{+}]_{o}$ = 0.10M

$[L]_{o}10^{3}/M$	$10^{3}k_{obs}/s^{-1}$
2.0	4.762
3.0	6.366
5.0	7.85
6.0	8.11
8.0	8.95

L = Glutathione λ = 430nm.

Temp 15°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	0.511
8.0	0.820
10.0	1.00
12.0	1.21
14.0	1.400

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	0.745
8.0	1.069
10.0	1.203
12.0	1.359
14.0	1.602

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	1.19
8.0	1.50
10.0	1.801
12.0	2.009
14.0	2.15

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	1.481
8.0	1.802
10.0	1.958
12.0	2.20
14.0	2.406

Temp 25°C

$[H^+]_o$ = 0.02M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
3.0	0.442
5.0	0.6794
8.0	0.9788
10.0	1.3125
12.0	1.6221

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
3.0	0.7077
5.0	0.9108
8.0	1.3125
10.0	1.6041
12.0	1.8629

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
2.0	1.01
3.0	1.10
5.0	1.25
6.0	1.57
8.0	1.71

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	$10^3 k_{obs}/s^{-1}$
2.0	1.54
3.0	1.65
5.0	1.85
6.0	2.14
8.0	2.20

Temp 30°C

$[H^+]_o$ = 0.04M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	1.229
8.0	1.805
10.0	2.204
12.0	2.888
15.0	3.438

$[H^+]_o$ = 0.06M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	1.805
8.0	2.447
10.0	2.917
12.0	3.417
15.0	4.125

$[H^+]_o$ = 0.08M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	2.406
8.0	3.039
10.0	3.358
12.0	3.671
14.0	4.44

$[H^+]_o$ = 0.10M

$[L]_o 10^3$/M	$10^3 k_{obs}/S^{-1}$
5.0	3.424
8.0	3.938
10.0	4.375
12.0	4.813
14.0	5.282

(a fact confirmed by the absorbance increase) the result obtained would be a reflection of the importance of a denominator term in the rate law. This trend was also observed in the reactions of chromium (VI) with the thioureas[146] and thiocyanate.[117]

There was no difference in the reaction rate when about 0.0416M Mn (II) was present in the reacting mixtures and also when all the reacting solution were degassed. From the data obtained the following reaction scheme can be postulated.

$$HLCrO_3 + H^+ \xrightarrow{k_1} Cr(V) \qquad (21)$$

$$HLCrO_3 + H_2L \xrightarrow{k_2} Cr(IV) \qquad (22)$$

From these reactions the rate law given by equation (23) may be derived.

$$-\frac{d[Cr(VI)]}{dt} = \frac{K[H_2L]\left(k_1[H^+] + k_2[H_2L]\right)}{1 + K[H_2L]}\,(Cr(VI)_{tot} \qquad (23)$$

$$= k_{obs}\,[Cr(VI)]_{tot} \qquad (24)$$

where $[Cr(VI)]_{tot} = [Cr(VI)]_o$

$$\therefore\ kobs = \frac{K[H_2L]}{1 + K[H_2L]}\left\{k_1[H^+] + k_2[H_2L]\right\} \qquad (25)$$

Rearrangement of equation (25) gives equation (26)

$$\frac{k_{obs}(1 + K[H_2L])}{K[H_2L]} = k_1[H^+] + k_2[H_2L] \qquad (26)$$

$\frac{k_{obs}(1 + K[H_2L])}{K[H_2L]}$, γ, evaluated using the

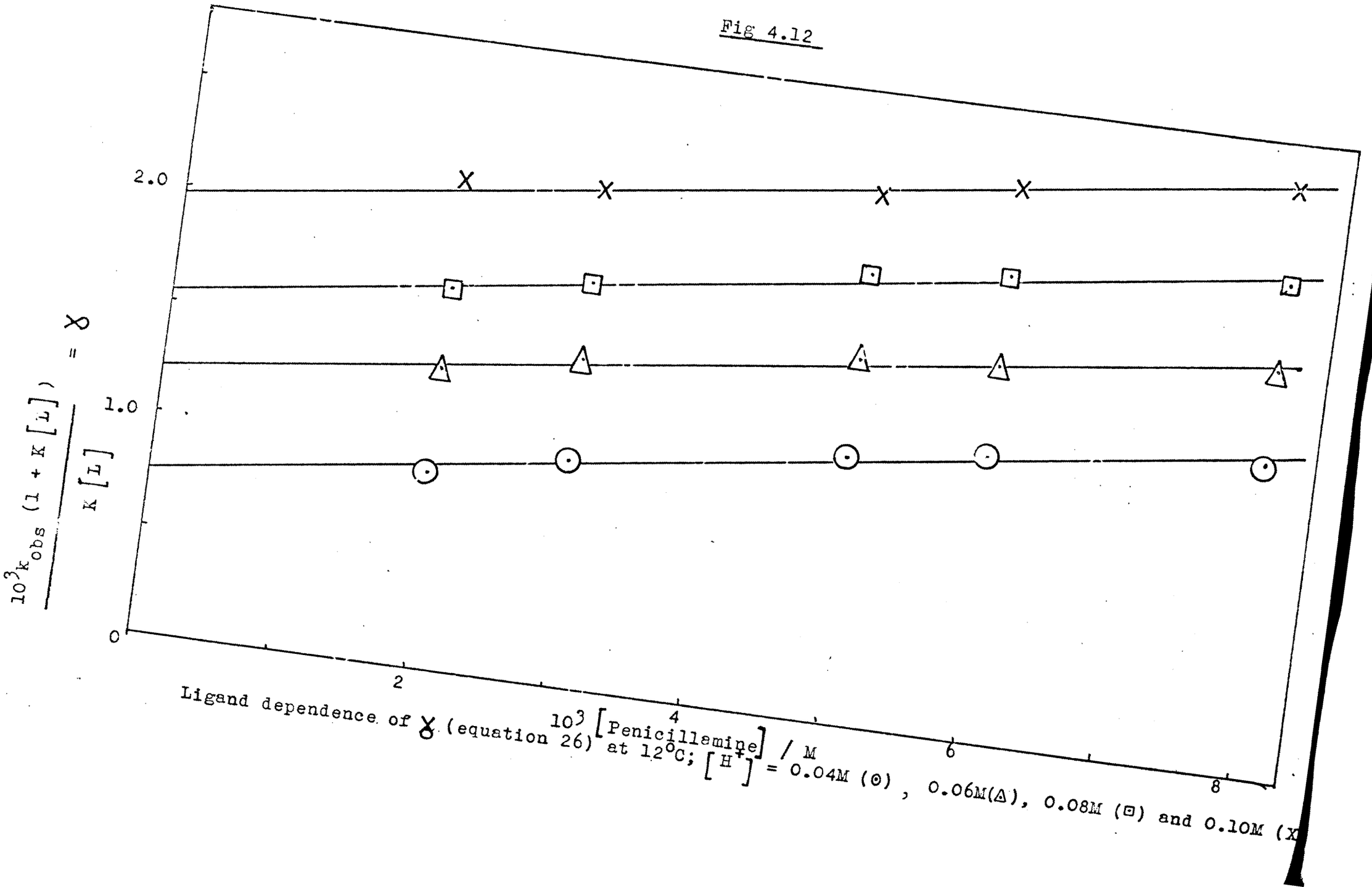
appropriate values of K in Table 4.2 was found to be a linear function of $[H_2L]$ (Fig 4.12 and 4.13). The slopes from such plots which yielded k_2 directly were found to be independent of the ligand concentrations in agreement with the scheme. The intercept was found to plot linearly as a function of $[H^+]_o$ in the case of penicillamine (Fig 4.14) and $[H^+]_o^2$ in the case of glutathione (Fig 4.15). k_1 was derived from such plots Temperature dependence of the rate data are illustrated in Table 4.6.

(c) Mechanism of the Redox Processes

Reaction (21) is part of a three consecutive one electron - transfer mechanism (already discussed) with the first of the three steps being rate - determining.

As can be seen from the values of the rate constants k_1 and k_2 in Table 4.6, the major route in these studies

Fig 4.12



Ligand dependence of γ (equation 26) at 12°C; $[H^+]$ = 0.04M (⊙), 0.06M(△), 0.08M (⊡) and 0.10M (X

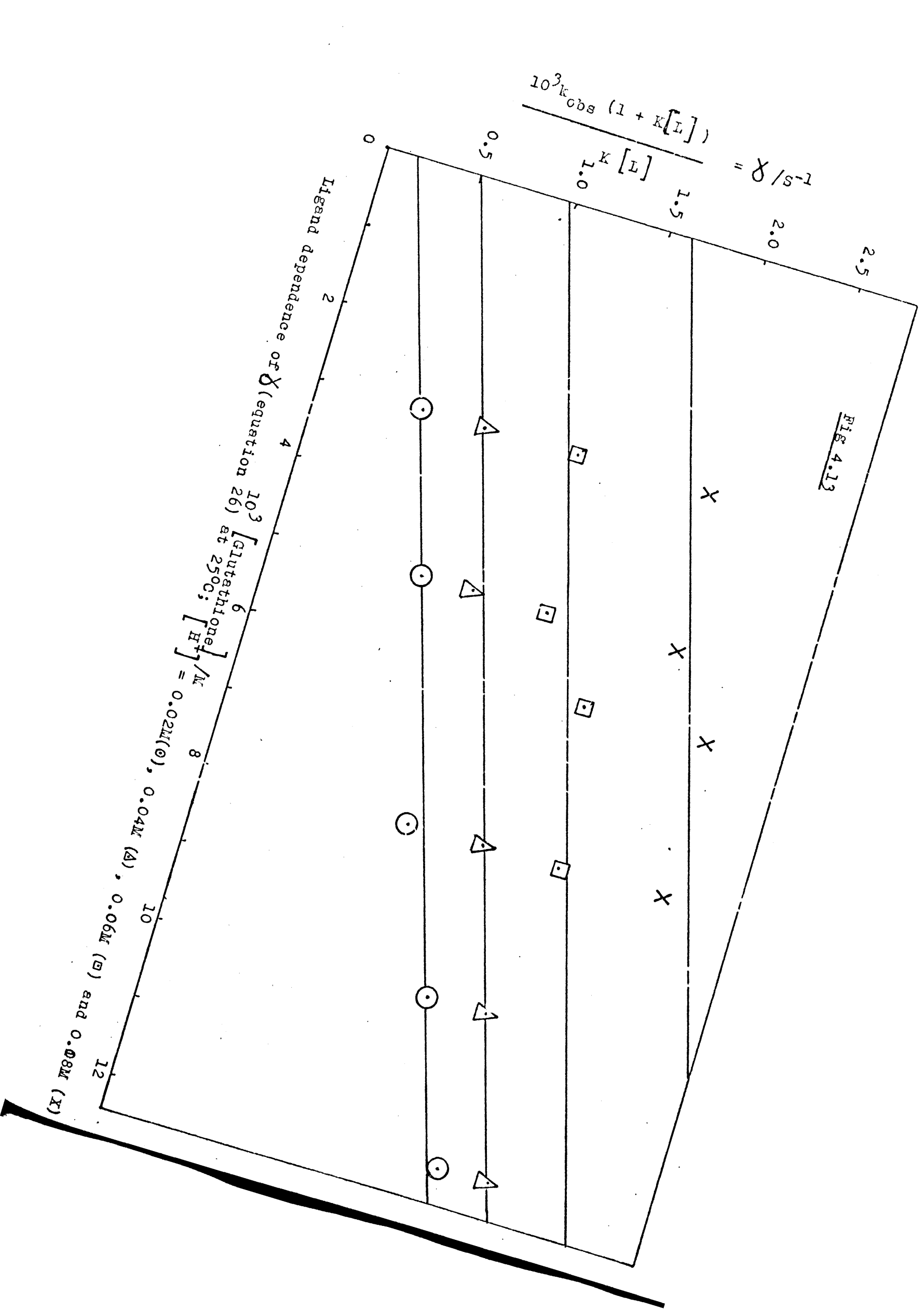
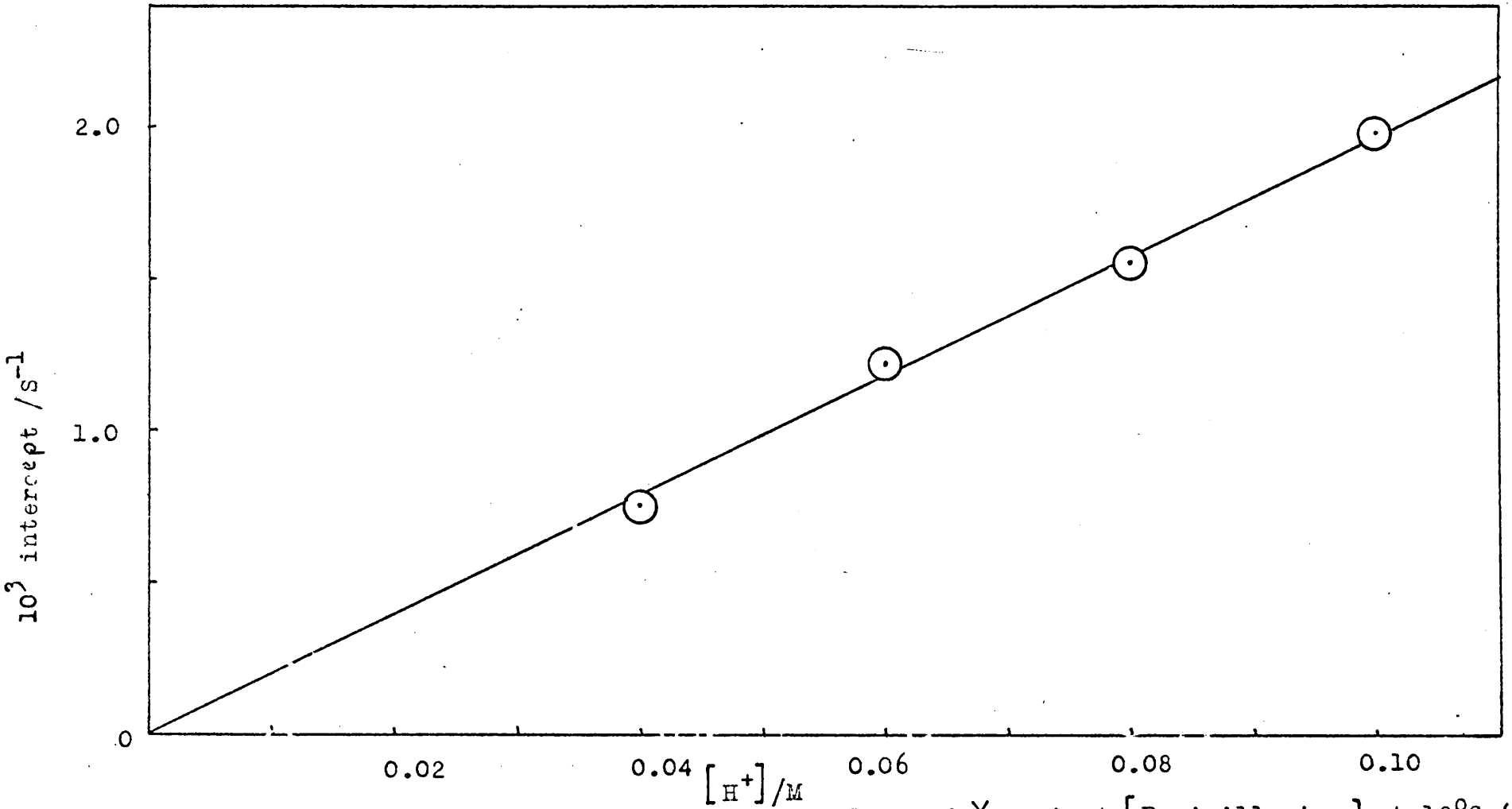

$10^3 k_{obs}(1 + K[L]) / K[L] = \gamma / s^{-1}$
0
0.5
1.0
1.5
2.0
2.5
Ligand dependence of γ (equation 26) at 25°C; 10^3 [Glutathione] = 0.02M (○), 0.04M (△), 0.06M (□) and 0.08M (X)
Ligand dependence or γ (equation 10^3 [Glutathione
10^3 [H+]/M = 0.02M(○), 0.04M (△), 0.06M (□) and 0.08M (X)
0
2
4
6
8
10
12

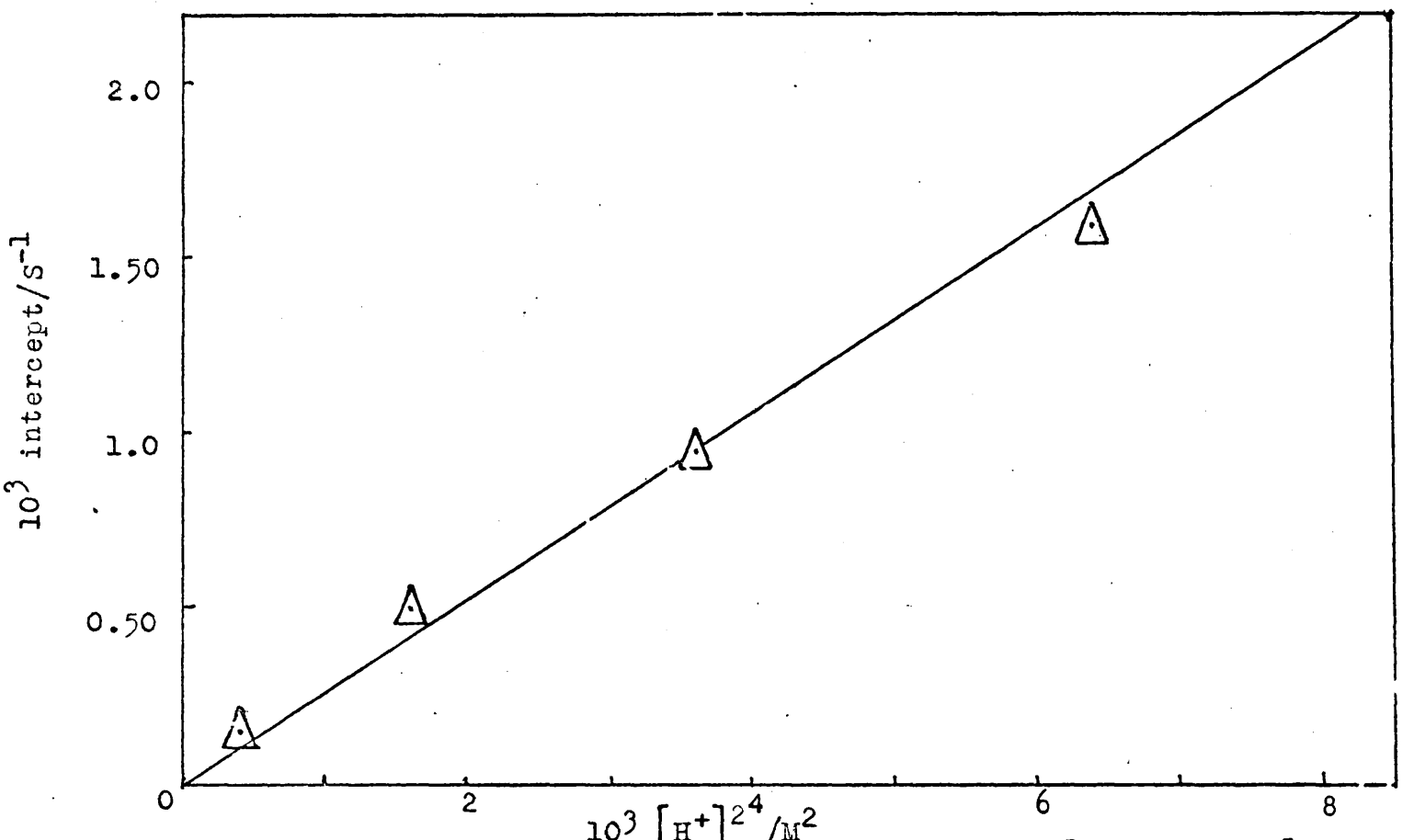
Fig 4.13

Fig 4.14



Hydrogen-ion dependence of intercept from plots of χ against [Penicillamine] at 12°C (equation 25)

Fig 4.15



Hydrogen-ion dependence of intercept from plots χ against [Glutathione] at 12°C (equation 25).

TABLE 4.6

Variation of the various constants for the redox reactions between chromium (VI) and the thiols (L) with temperature.

L = Penicillamine

$T^{o}C$	$10^{2}k_{1}/l^{2}mol^{-2}s^{-1}$	$10^{2}/k_{2}l^{2}mol^{-2}s^{-1}$
12.0	1.95±0.2	8.0±0.5
17.0	2.90±0.5	11.8±0.5
25.0	5.7±1.0	14.3±1.0
ΔH^{*}/Kcal mol^{-1}	14.1±3	9.0±2
ΔS^{*}/cal $K^{-1}mol^{-1}$	-16.7±5	-32.5±6

L = Glutathione

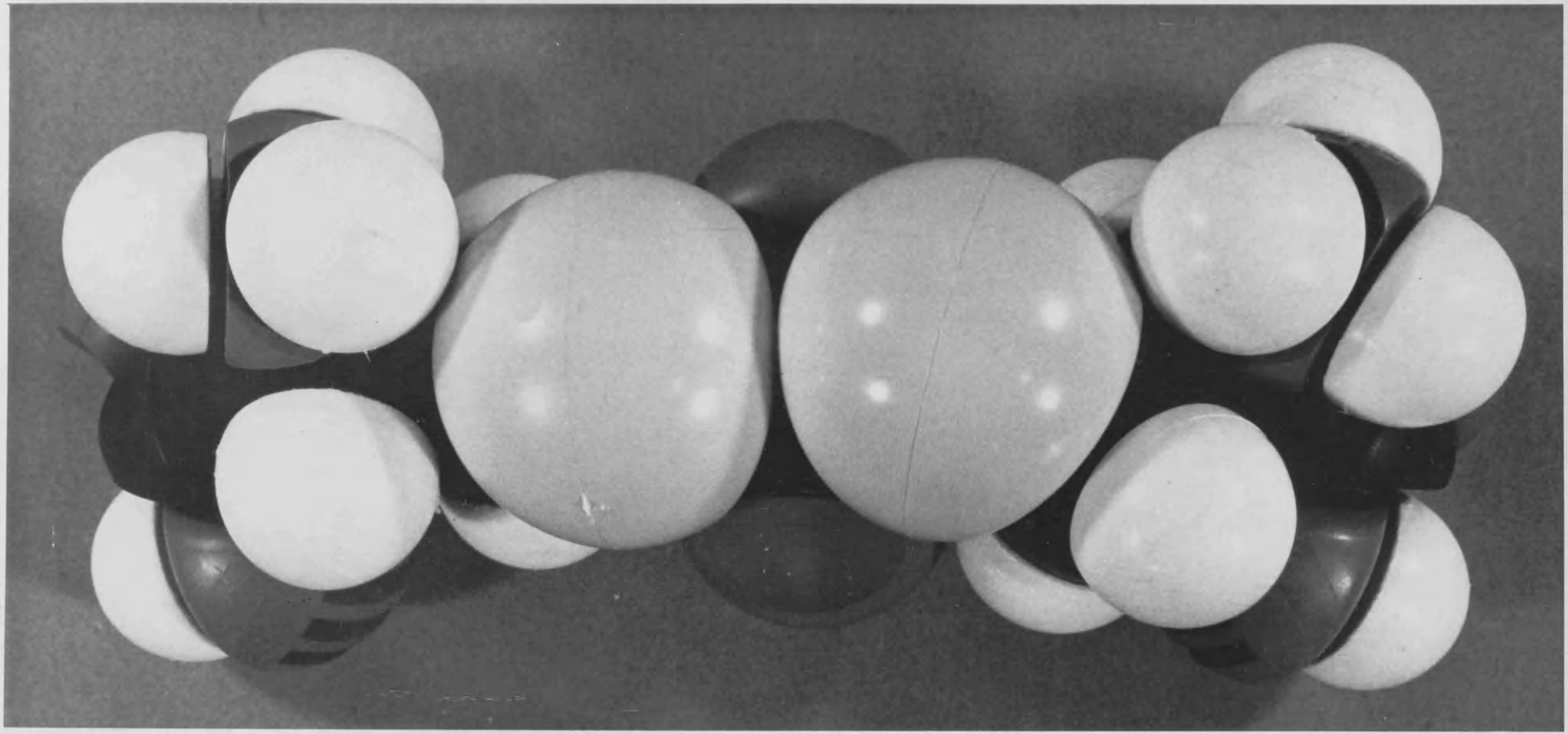
$T^{o}C$	$10^{2}k_{1}/l^{2}mol^{-2}s^{-1}$	$10^{2}/k_{2}l^{2}mol^{-2}s^{-1}$
15.0	11.2±2	9.7±0.2
25.0	25.0±4	12.1±0.4
30.0	26.6±5	21.2±0.6
ΔH^{*}/K cal mol^{-1}	11.0±3	6.9±2
ΔS^{*}/cal $K^{-1}mol^{-1}$	-24.3±7	-39.7±5

as with similar reactions involving thioureas,[146] cysteine,[134] thiocyanate[117] and thiosulphate[110] involve second order ligand dependences. The significance of such second - order processes in the expansion of the chromium co-ordination number from 4 to 6 has been discussed[29] (see also chapters II and III). The low energy pathway provided by the formation of the incipient disulphide may also be a factor. The evidence obtained in these studies that the product disulphide is co-ordinated to Cr(III) supports this latter view.

Chromium (IV) is thought to be an important intermediate in these reactions and regardless of whether it is formed by way of two consecutive one electron transfer, equation (21), or through an activated complex containing two molecules of the ligand bonded to chromium in the transition state (shown for cysteine in fig 4.16 ; reaction 22), reduction to chromium (III) product is by way of one equivalent oxidation of the ligand. The free radical produced as a result of this step is thought to dimerise.

Mn(II) which has successfully been used as a trapping agent for chromium (IV) has no effect on the reaction rate in these studies. This would tend to eliminate the participation of a second chromium (VI) in the subsequent reduction of the intermediate chromium (IV) to chromium (III) complexes and lend support to the theory that it is the ligand which is

Fig. 4.16



involved in this step.

In conclusion, the oxidation reactions involving penicillamine, glutathione and β - mercaptoethylamine proceed with the formation of a complex as the first - step in each case. This is similar to previous observations of reactions of chromium (VI) with $S_2O_3^{2-}$ (ref 110), HSO_3^- (ref 101), thiourea (ref 146), thiocyanate[117], cysteine[134] etc. Second - order dependence of the rate on ligand concentration was also observed as the major route in the oxidation of these ligands, a fact which is now an established feature of the reduction of chromium (VI) by sulphur containing ligands. However, product patterns, although similar to those found for cysteine[134] which is structurally related to the ligands, differ from those of thiourea and thiocyanate where the ligand and not the product is co-ordinated to chromium (III).

Before the mechanism of these reactions can be established with certainty more work is required in (a) the characterisation of the chromium (III) product complexes especially finding a reliable method which is capable of determining the low sulphur content of these species, (b) trapping and identification of the radicals and (c) the use of E.P.R. in monitoring the chromium (V) formed (if any).

C H A P T E R V

THE KINETICS OF THE ELECTRON TRANSFER BETWEEN THE 12 - TUNGSTOCOBALTATE (III) ANION AND THE THIOUREAS IN AQUEOUS SOLUTION.

Introduction

Earlier investigations of the reactions of thiourea and its N - substituted derivatives with chromium (VI)[146] revealed the formation of an intermediate complex in each case, as the first step in the overall reduction of the oxidant to the stable chromium (III) complexes. Isolation and characterisation of these product - species was thought important in the elucidation of the mechanisms of these oxidation reactions. However, in view of the experimental difficulties which often accompany this procedure especially in the reaction of chromium (VI) with some thiols referred to in the preceding chapter, it was thought desirable to study the reaction of the thioureas with a one - electron oxidant where the possibility of an inner - sphere complex formation is highly unlikely. It was also reasoned that if a ligand intermediate is formed, it would be a free radical and the free radical - co-ordinated radical ambiguity observed for some systems[148,149] and also in the chromium (VI) oxidation of some thiols (see chapter IV) would not exist.

The first complex ion to be used as an oxidant was the tris - (1,10 - phenanthroline) iron (III) species because of its substitution inertness[150] and preliminary investigations[151] of the reactions of this oxidant with the thioureas reveal a first - order dependence of the rate on ligand concentrations up to a 20 - fold excess or more

in some cases, followed by a second - order dependence. A similar result was obtained by Carlyle[152] in the kinetic studies of the electron transfer between HSO_3^- and tris - (1, 10 - phenanthroline) iron (III) ions.

Because of the unexpected observations made in the above investigations and in particular the possibility of a dimeric species of the oxidant[150,152] being one of the active species in solution, which would have to be included in the kinetic scheme, it was decided instead to study the reactions of 12 - Tungstocobaltate (III) anion. It was thought that the bulky tungsten - oxygen cages surrounding the tetrahedral cobalt atom would eliminate the feasibility of a direct complex formation between the cobalt and the thioureas, thereby giving rise tO simple electron exchange reactions with the stable 12 - Tungstocobaltate - (11) anion and the disulphide of the thioureas as the products.

There are very few reports in the literature of the electron exchange reactions involving these heteropoly complexes. However, the kinetics of the electron exchange between the 12 - Tungstocobaltate (11) and the 12 - Tungstocobaltate (III) anions have been studied in aqueous solutions.[153] An outer-sphere type of mechanism was postulated for the system and it is of interest to see how the present investigations agree with this scheme.

Experimental

(a) Preparation

Reagent grade chemicals were used without further purification for the preparation of the potassium salt of 12 - tungstocobaltate (11), $[Co^{II}O_4W_{12}O_{36}]^{-6}$ hereafter designated as anion I, by the method of Baker and McCutcheon.[154] The 12 - tungstocobaltate (III), $[Co^{III}O_4W_{12}O_{36}]^{-5}$ anion (II), was prepared electrolytically as follows. An unknown quantity of anion I was dissolved in about 150ml of 0.5M $HClO_4$ and placed in the anode compartment of an electrolytic cell. The other compartment also contained 0.5M $HClO_4$. The electrolysis was carried out using two bright platinum electrodes with an applied potential of 10V. As the electrolysis progressed, there was a gradual change of the colour of the solution in the anode compartment from green to yellow. When this process was completed, the yellow $[Co^{III}O_4W_{12}O_{36}]^{-5}$ solution was transferred to a stoppered conical flask and stored in the fridge overnight. White crystals of potassium perchlorate were observed in the conical flask the following day and these were filtered off leaving a clear yellow solution.

The remaining potassium ions in the stock solution were replaced with lithium ions by the use of Dowex 50W - X12 Cation - exchange resin. The procedure

adopted was as follows. The cation exchange resin in the hydrogen form, was placed in a column 40cm long and about 3cm internal diameter. A fairly concentrated solution of lithium sulphate was allowed to run slowly through the column after which it was flushed through several times with distilled water until it was sulphate free. The prepared solution of anion II was then allowed to pass down the column at a very slow rate with the lithium ions on the resin being displaced by the potassium ions in the solution. The above procedure was repeated twice using a fresh cation exchange resin. on each elution.

The removal of potassium ions was necessary for two reasons. Firstly, under ClO_4^- ion concentration of 1.0M precipitation of potassium perchlorate may occur and this is likely to interfere with the transmission of light through the solution in the observation tube. Secondly, since the presence of potassium ion had been found[153] to increase the rate of electron - exchange between anions I and II, the use of lithium was therefore desirable to minimise this effect based presumably on the bigger size of the potassium ions.

(b) Analysis

The concentrations of the stock solutions of anion II were determined by both spectrophotometric and

potentiometric titrations with ferrous ammonium sulphate which quantitatively reduces anion II to anion I.

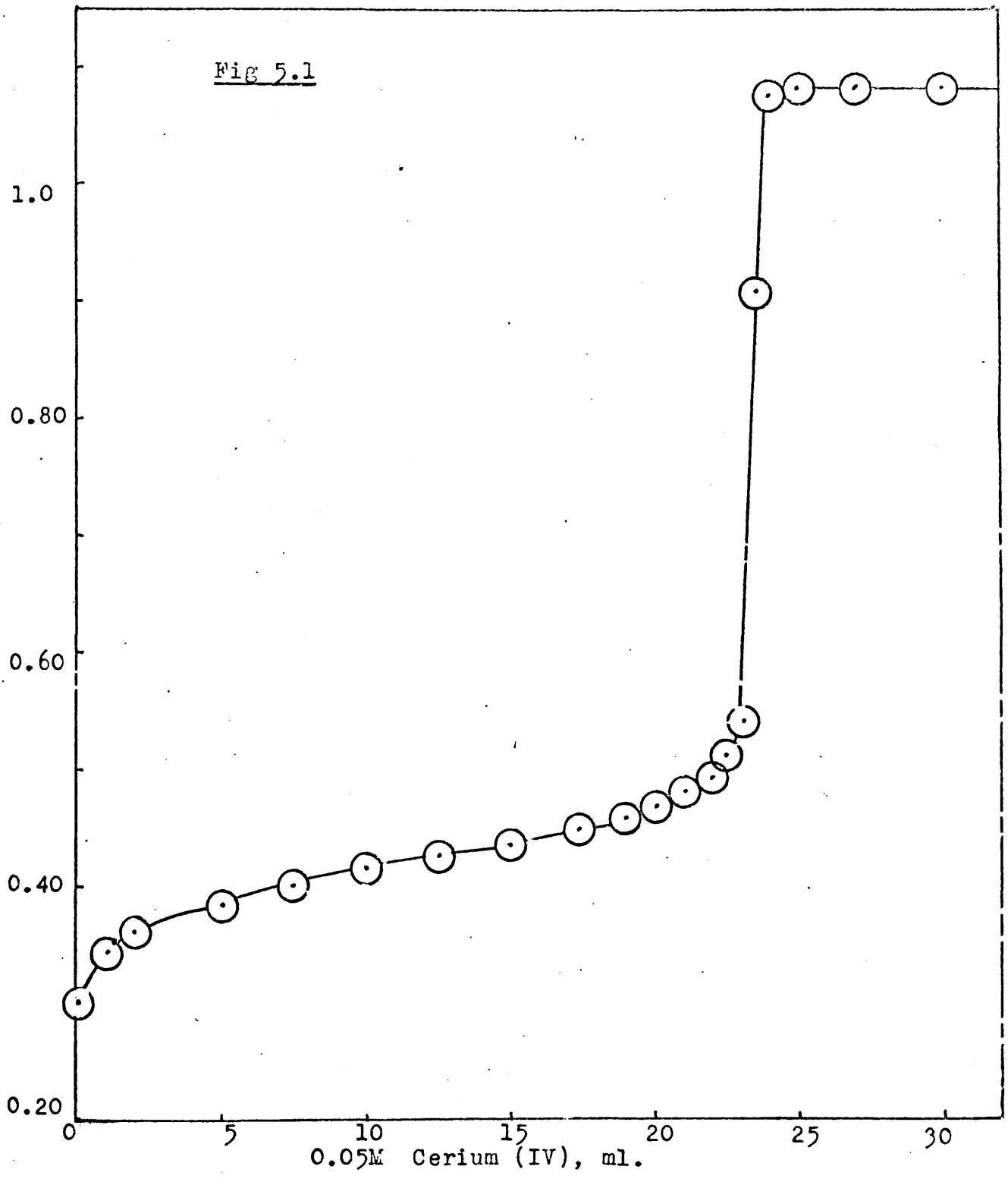
The ferrous ammonium sulphate used was standardised by potentiometric titration as follows. 20ml of 0.05M ferrous ammonium sulphate prepared in about 1M H_2SO_4 was measured out accurately into a 100ml beaker. Two electrodes, one a calomel electrode as reference and a platinum electrode as the indicator electrode were placed in the beaker. The electrodes were attached to a pH meter (Vibret 46L). Small volumes of a standard 0.05M Ceric ammonium sulphate solution were then added to the solution in the beaker at intervals. After each addition, the solution was stirred for about 2-5 minutes using a magnetic stirrer and the e.m.f. of the solution was then recorded. A graph of E(V) against volume of cerium (IV) added was plotted (Fig 5.1) and the concentration of ferrous ammonium sulphate evaluated. This was confirmed by a spectrophotometric titration using a standard solution of potassium dichromate. The two results agree to $\pm 1\%$.

The saturated calomel electrode has a potential of 0.246 V when compared with the standard hydrogen electrode. The voltage measured represents the difference in potential of the indicator and reference electrode:

$$E_{meas} = E_{ind} - E_{ref} \qquad (1)$$

The potential of the indicator electrode can, therefore be

Fig 5.1



Potentionmetric titration curve for Fe(II) and Ce(IV) in 1.0M H_2SO_4 .

calculated from the measured voltage by substituting the potential of the calomel reference electrode into the equation above:

$$E_{ind} = E_{meas} + 0.246 \qquad (2)$$

From equation (2), it is possible to calculate the equivalence point potential for the titration of Fe(II) with Ce(IV).

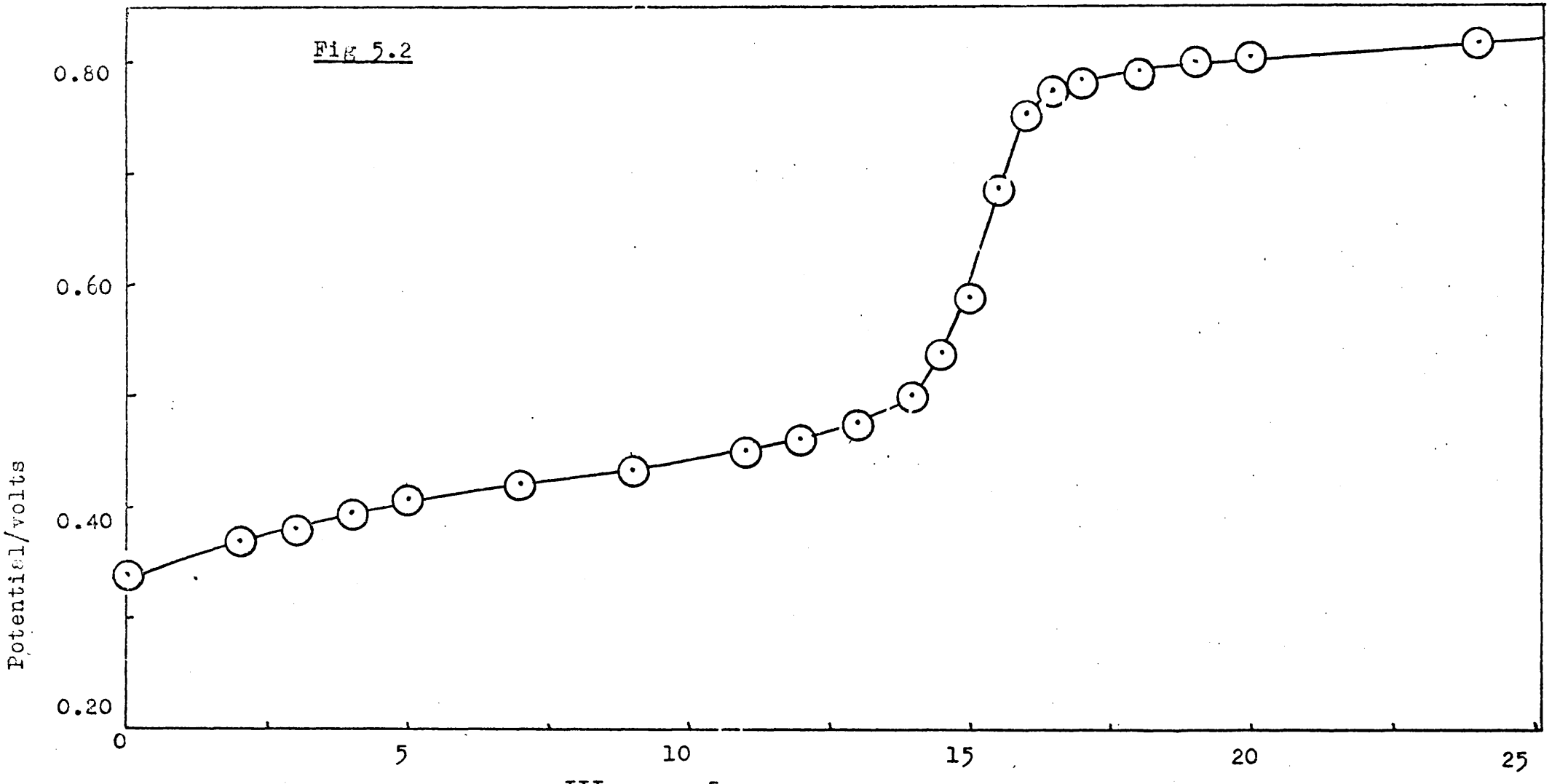
$$E_{equiv} = 0.800 + 0.246$$
$$= 1.046V$$

The value obtained experimentally is comparable to the theoretical value of 1.105V.

Potentiometric titration of anion II with the standardised ferrous ammonium sulphate was carried out in exactly the same manner as outlined above using 10ml of 5.85×10^{-3}M Fe(II) solution with various volumes of anion (II) stock solution. The titration curve from which the concentration of the anion II was evaluated is as shown in Fig 5.2.

The spectrophotometric titration method for determining the concentration of anion II involves mixing about 2ml of the stock solution of the oxidant with various volumes of 1.04×10^{-3}M Fe(II) solution in different 10ml volumetric flasks and making each solution up to the mark with distilled water. After shaking, the flasks were kept aside for some time to ensure that the reaction had gone to completion. The spectrum of each solution

Fig 5.2



Volume of $Co^{III}O_4W_{12}O_{36}^{-5}$ stock solution added.

Potentiometric titration curve for anion (II) and Fe(II).

was obtained using an SP 800 spectrophotometer and the optical density at λ = 390nm for each solution was plotted against volume of Fe(II) added. A typical titration curve obtained for a different concentration of anion (II) is presented in Fig 5.3. Results obtained from the two methods agree to within $\pm 2\%$.

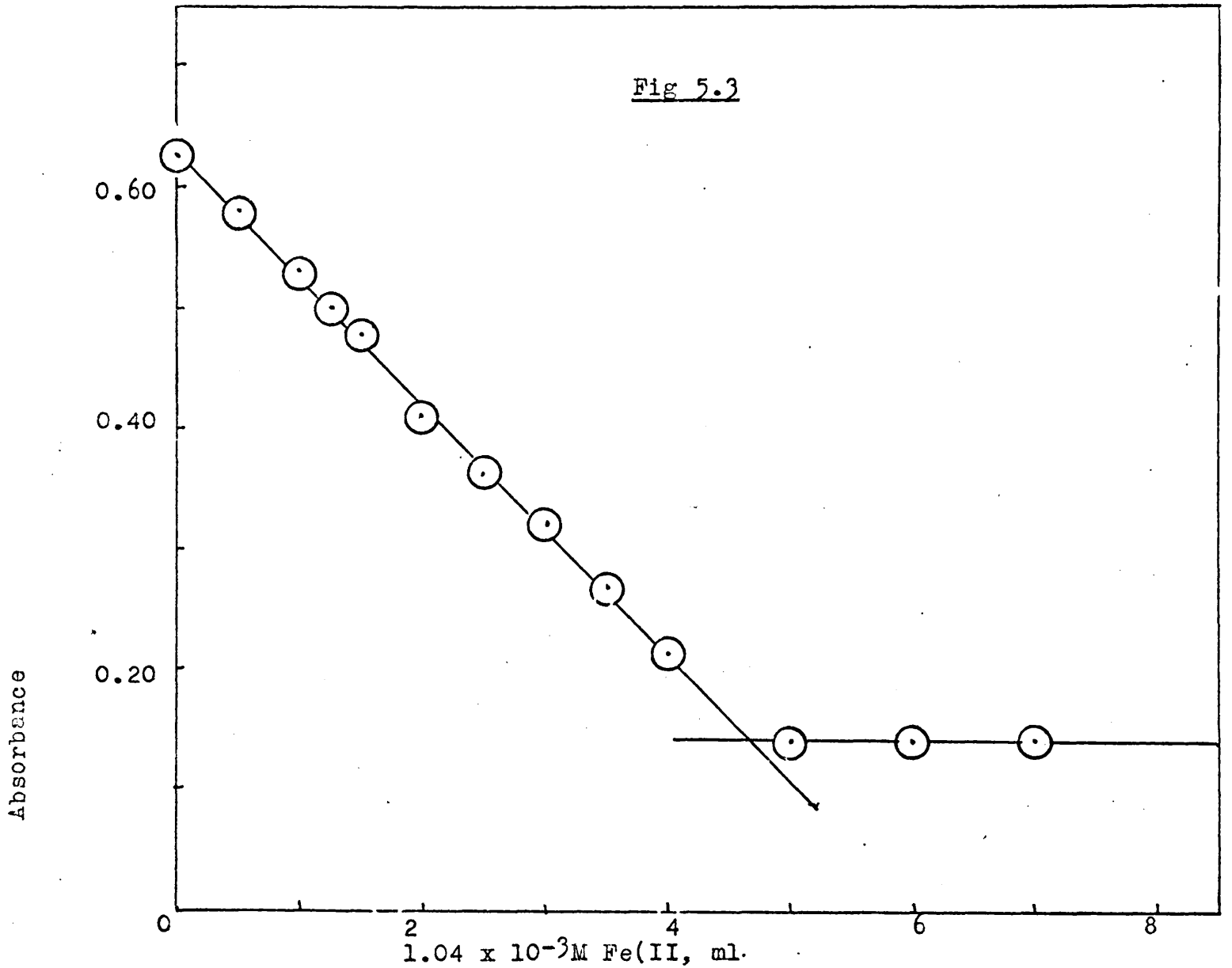
The reduction potential of the anion II - anion I couple was determined by potentiometric titration of (a) anion II with iron (II) and (b) Ce(IV) with anion (I). The experimental procedure was as described for Ce(IV) - Fe(II) redox reaction earlier. In the Fe(II) - anion (II) measurement, 10ml of 5.85×10^{-3}M Fe(II) was titrated against 3.82×10^{-3}M anion II while an unknown concentration of anion I was titrated against 5×10^{-3}M Ce (IV). The titration curves obtained for both (a) and (b) are shown in figs 5.2 and 5.5 respectively.

The potential at the equivalence point for any redox reaction is given by

$$E_{equiv} = \frac{n_A E^o_A + n_B E^o_B}{n_A + n_B} \qquad (3)$$

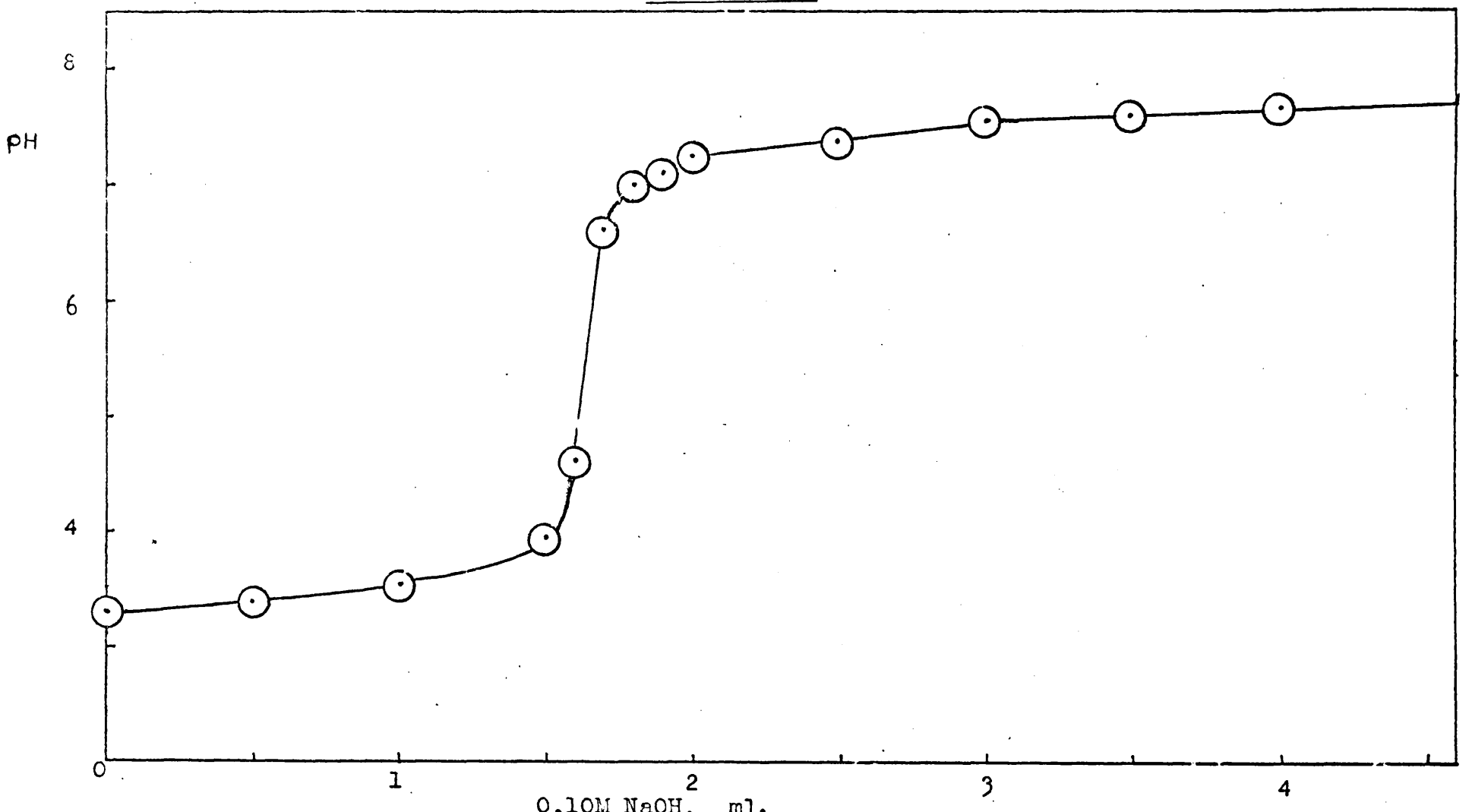
where E^o_A refers to the redox couple of the oxidizing agent, n_A is the electron change in this half reaction, E^o_B refers to the redox couple of the reducing agent and n_B is the corresponding electron change. From the titration

Fig 5.3

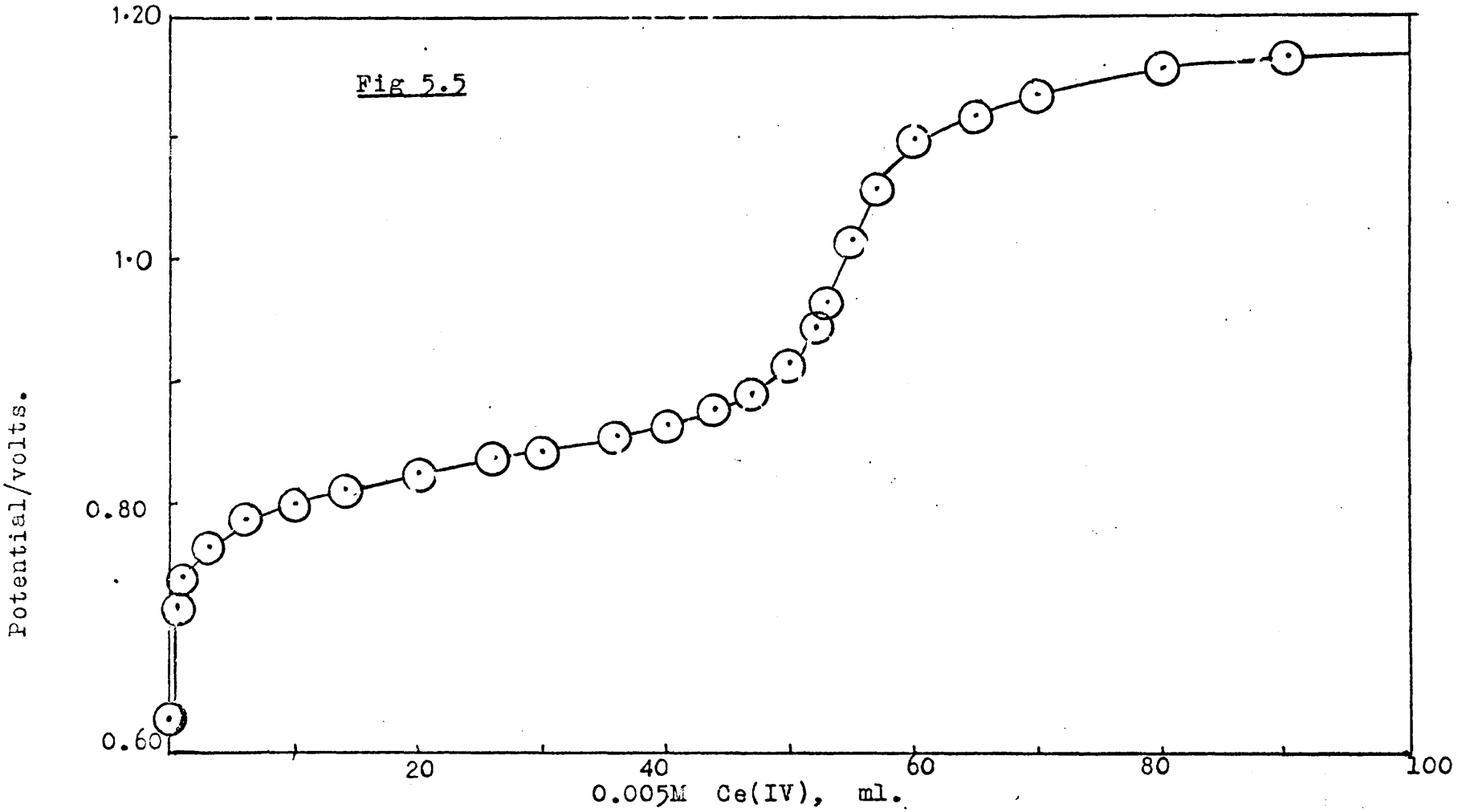


Spectrophotometric titration curve for anion II and Fe(II) at λ = 390nm

Fig 5.4



pH titration curve for determining the hydrogen - ion concentration of anion II stock solution.



Potentiometric titration curve for $Co^{II}O_4W_{12}O_{36}^{-5}$ (anion I) and Ce(IV).

curves in figs 5.2 and 5.5 the E_{equiv} in both cases can be obtained and from the known E^{o} values for iron (II) and Cerium (IV) the redox couple of anion II and anion I can be calculated using equation (3). This value was infact found to be 1.03±0.01 V which is close to the literature value of 1.0 V (ref 155).

The acid strength of the stock solutions of anion II were determined by pH titration using a standard solution of 0.10M NaOH. The pH meter used was the same Vibret 46L as was used for e.m.f. measurements above, only that in this case, the platinum electrode was replaced by a glass electrode. Typical pH titration curve obtained is as shown in Fig 5.4. The acid strength of the stock solutions in all cases were between 0.05 and 0.10M and these values were taken into consideration in the hydrogen ion dependence studies. The complex anion II stock solutions were stored in a refrigerator and were found to be quite stable under this acidity range for several weeks.

The thioureas used in these investigations were recrystallised as outlined in chapter III. Hydrogen ion concentration was varied using perchloric acid (Analar) while the ionic strength was maintained constant with lithium perchlorate prepared as described in chapter I.

(c) Stoicheiometry

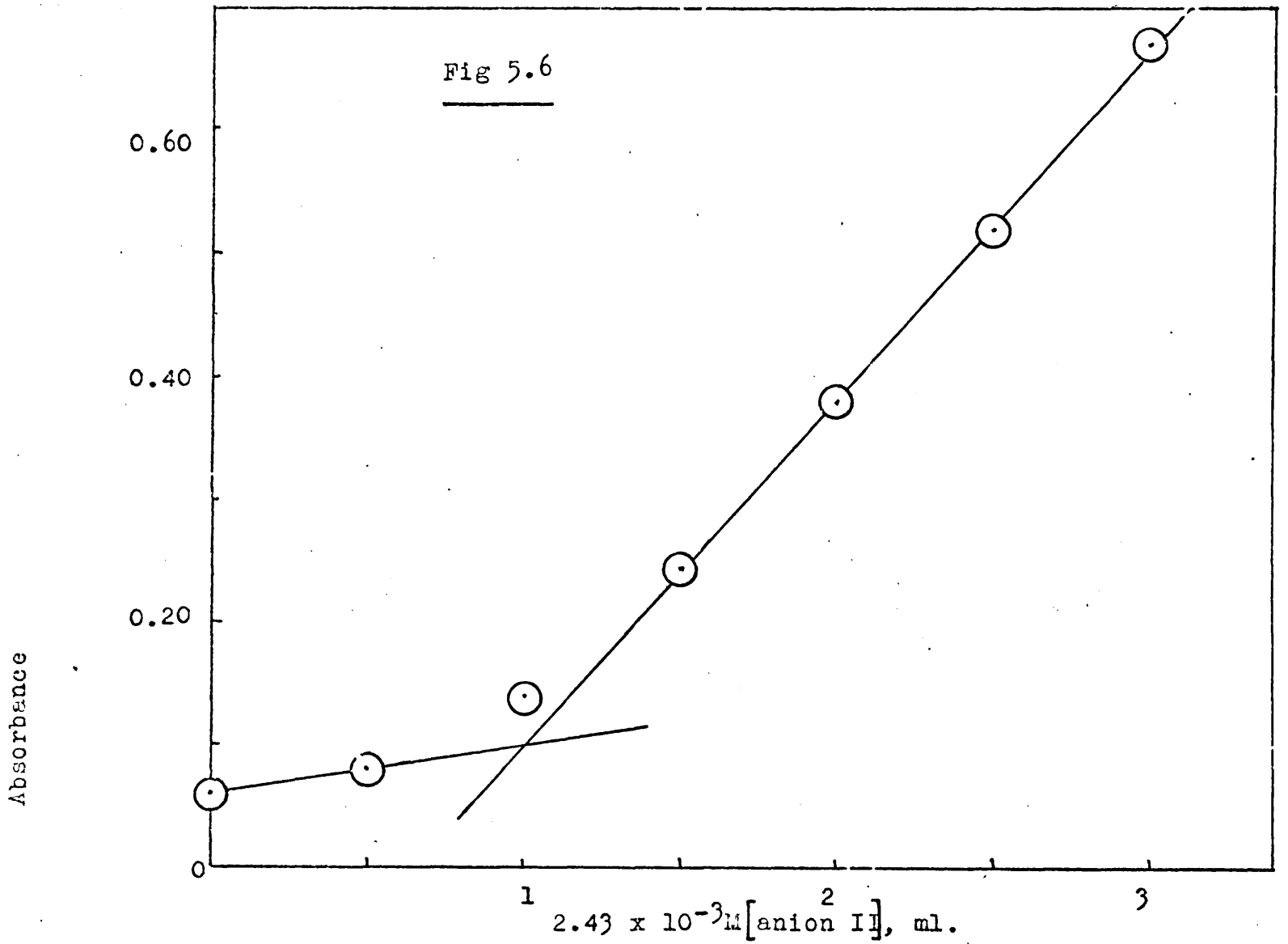
The stoicheiometries of the reactions of

$[Co^{III}O_4W_{12}O_{36}]^{-5}$ (anion II) with thiourea, N - methylthiourea and NN^1-ethylenethiourea were determined both spectrophotometrically and by potential measurements. These two methods have been discussed in detail earlier.

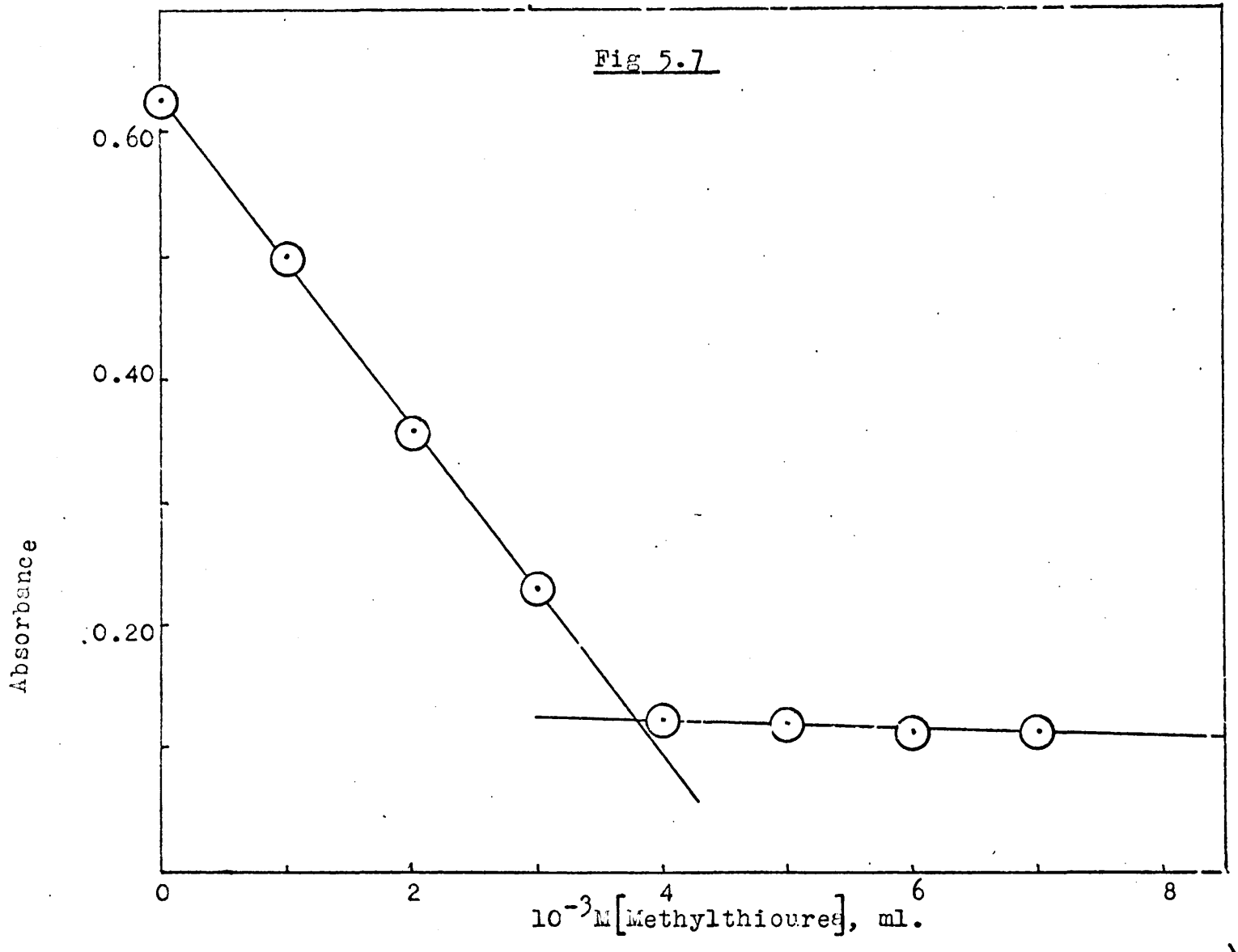
In the spectrophotometric titrations involving excess ligands, 2mls of 3.418×10^{-3}M anion (II) were mixed with various volumes of 3×10^{-3}M ligand and made up to 10ml solution with distilled water; while in excess complex anion II, 2ml of 10^{-3}M ligand was involved. From the results obtained representative curves of which are shown in Figs (5.6-5.8), a complex: ligand ratio of 1:0.95±0.03 was obtained for the reactions involving thiourea and methylthiourea with anion II. This value was confirmed by potentiometric titrations (Figs 5.9 - 5.11). However ethylenethiourea was observed to behave differently using both methods as illustrated in Figs (5.8 and 5.11). This unusual behaviour of ethylenethiourea towards anion II might be a kinetic effect rather than a thermodynamic one. A rough estimate of the equilibrium constant for the reaction (4) show that the reaction is expected to go extensively to completion.

$$2\,[Co^{III}O_4W_{12}O_{36}]^{-5} + 2L \rightleftharpoons 2\,[Co^{II}O_4W_{12}O_{36}]^{-6} + 2L^1\text{-}L^1 \qquad (4)$$

However, the redox potential of thiourea[156] and substituted

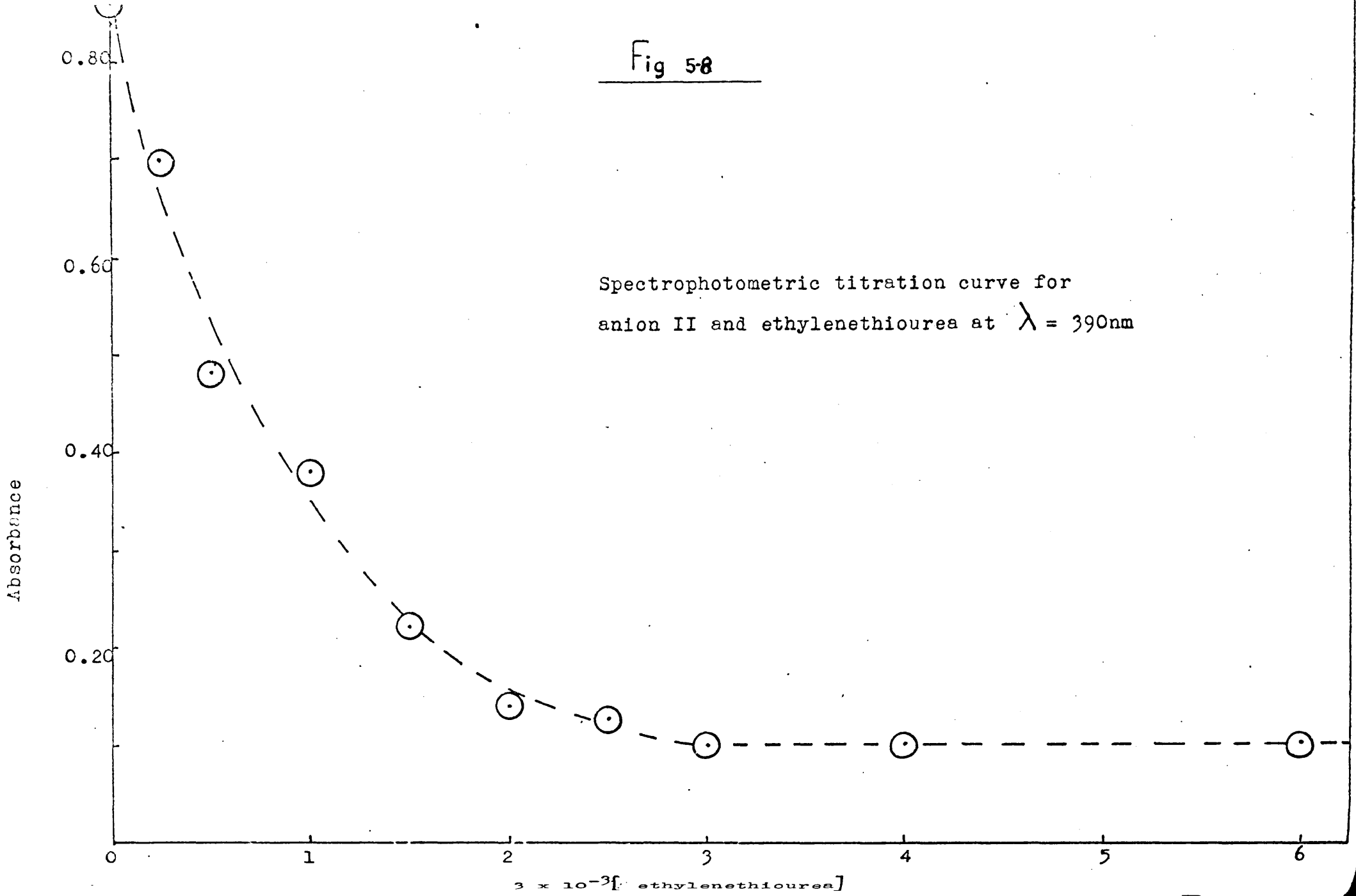


Spectrophotometric titration curve for anion II and thiourea at λ = 390nm.

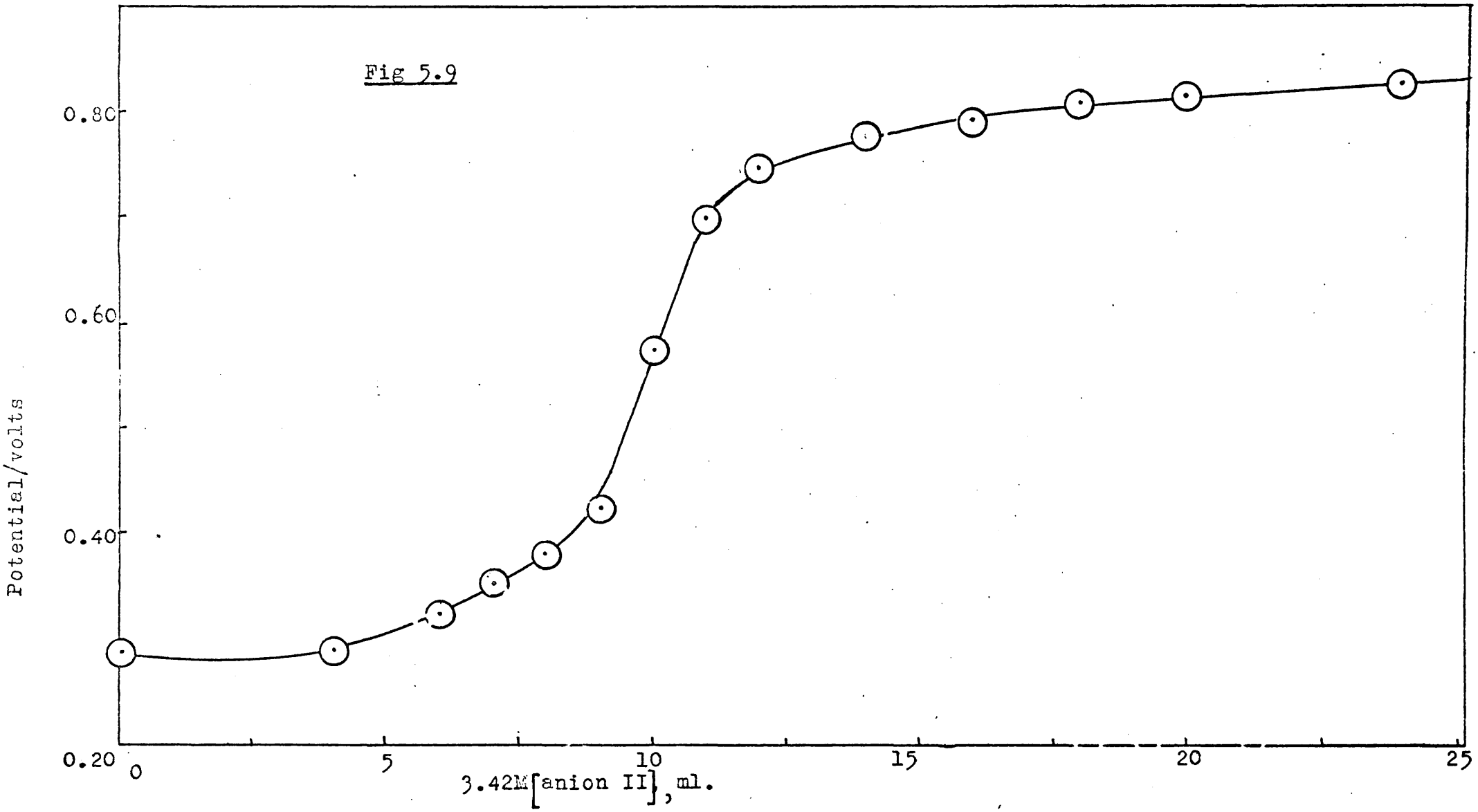


Spectrophotometric titration curve for anion II and methylthiourea at λ=390nm.

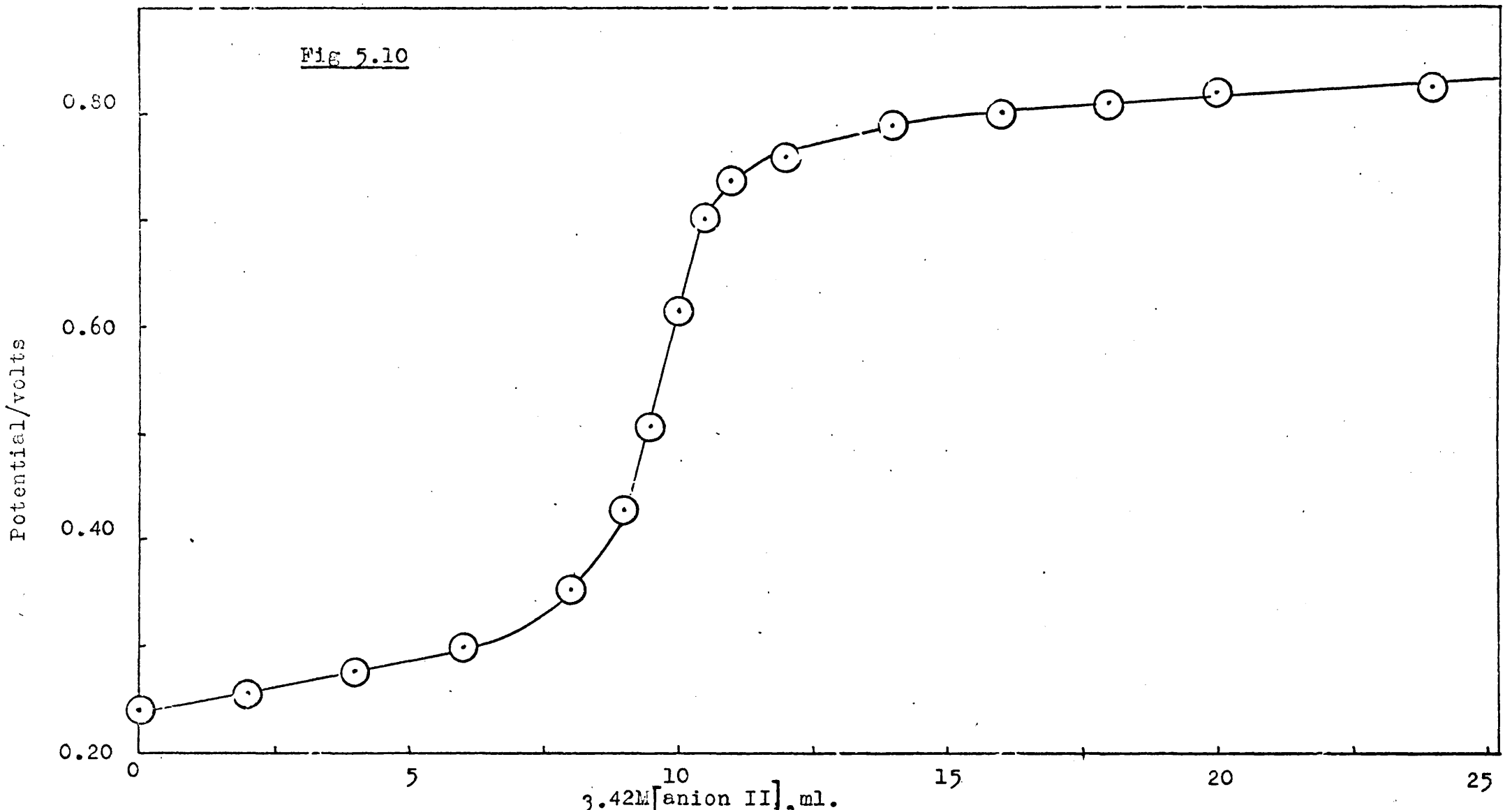
Fig 5-8



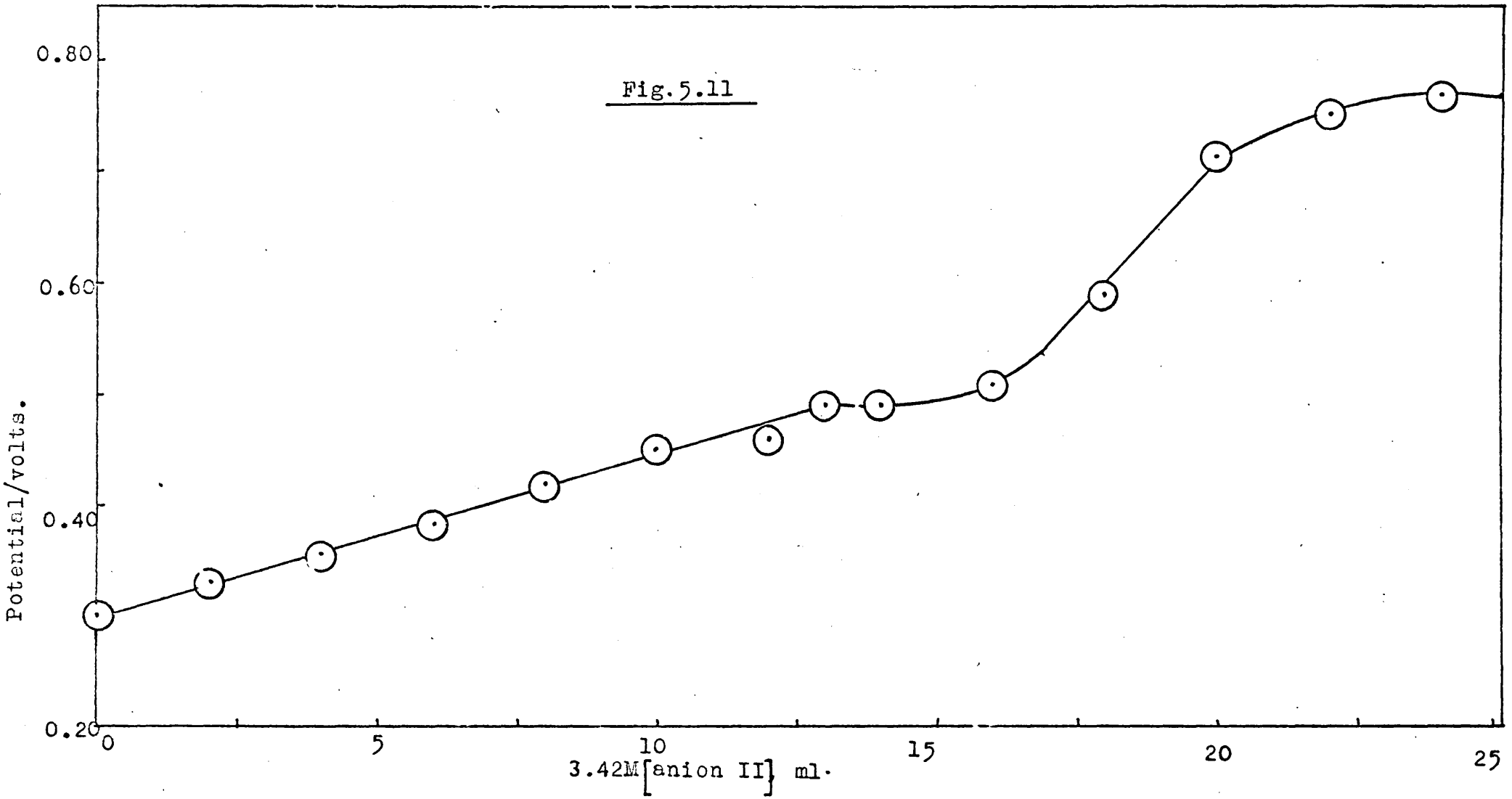
Spectrophotometric titration curve for anion II and ethylenethiourea at λ = 390nm



Potentiometric titration curve for anion II and thiourea.



Potentiometric titration curve for anion II and Methylthiourea.



Potentiometric titration curve for anion II and ethylenethiourea.

thiourea[157] - disulphide systems had been measured previously and no such effect was reported.

From the potentiometric titration curves (Fig 5.9 - 5.11) the different potentials at equivalence points were obtained and using equation (2) in conjunction with equation (3) E^{o} for the ligand - disulphide couples were obtained. Although these values were slightly higher by $\leq 10\%$ than those reported in the literature[156,157] they were in the same order of magnitude i.e. ethylenethiourea > thiourea $\geq$ methylthiourea.

(d) Kinetics

The anion II spectrum exhibits a maximum at λ = 390nm in the visible region. Consequently its redox reactions with thiourea, N - methylthiourea and NN^{1} - ethylenethiourea were studied at this wavelength using the stopped - flow apparatus described in chapter 1 with a dead time of the order of milliseconds. Pseudo - first - order rate constants were derived from transmission curves using a Noval 1200 computer, by the method given in chapter I.

The slower redox reactions at the lowest temperature studied (8.7°C) were monitored using the hand - driven stopped - flow system which is also described in chapter I.

The concentration of the reactants employed in these studies are as follows: [anion II] = 2×10^{-4}M,

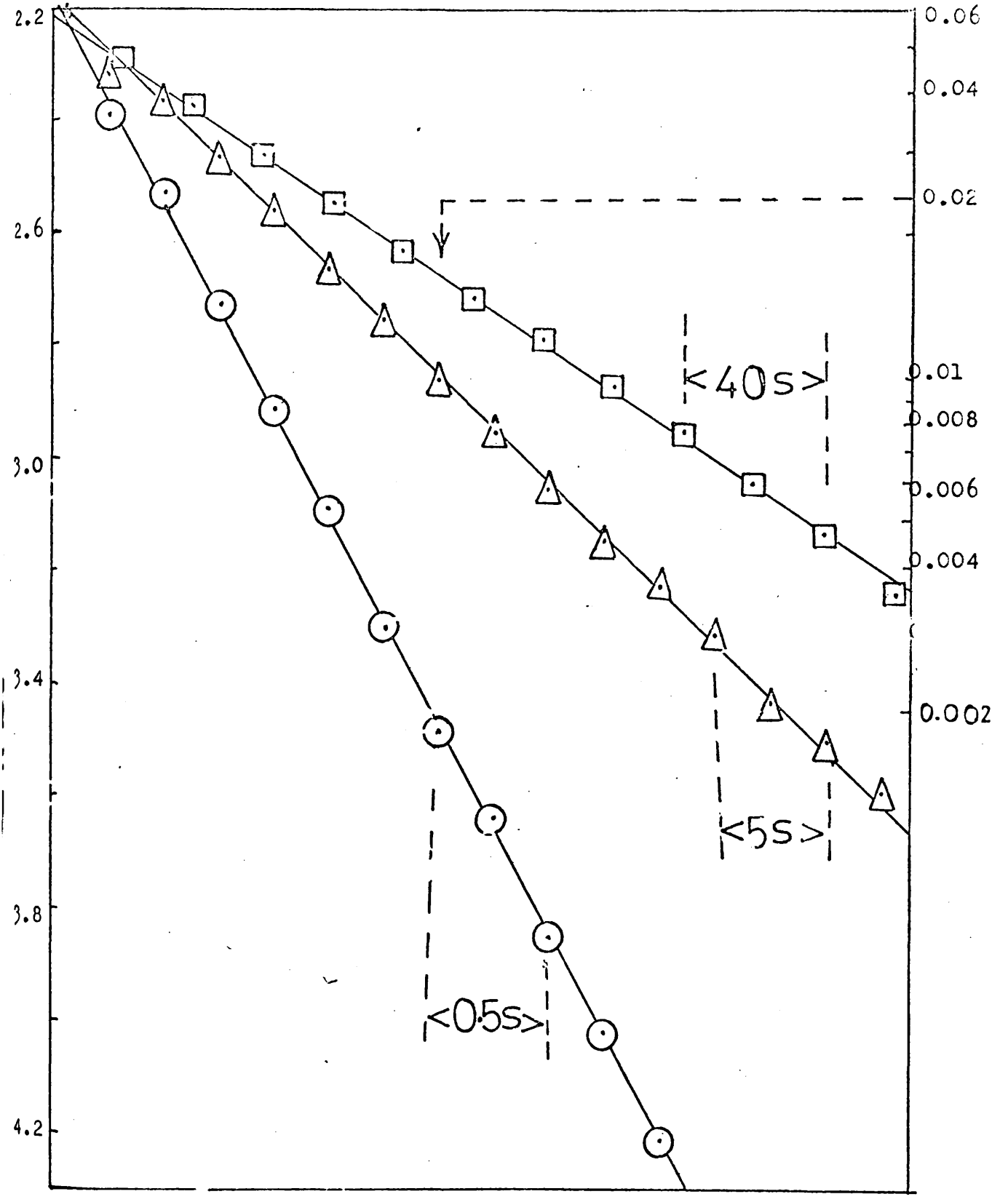
$[\text{Ligand}] = (1.5\text{-}15) \times 10^{-3}$M and $[H^+]_o = (0.10\text{-}1.0)$M. The ionic strength of the medium was maintained constant at 1.0M with lithium perchlorate.

RESULTS AND DISCUSSION

All the kinetic data were obtained using an excess of the ligand. Comparison of the initial absorbances in these kinetic investigations with those for the anion II when no ligand was present showed no significant difference. This is an indication that no detectable intermediate was formed. Plots of $\ln(OD_\infty - OD_t)$ as a function of time were linear to about 80%, usually more at higher temperatures (Fig 5.12) and pseudo-first order rate constants, k_{obs}, were obtained from the slope of such plots. The variation of this parameter with temperature is tabulated in Table 5.1. Within experimental error, the rate constants were found to be independent of the hydrogen ion concentrations used (see Table 5.1).

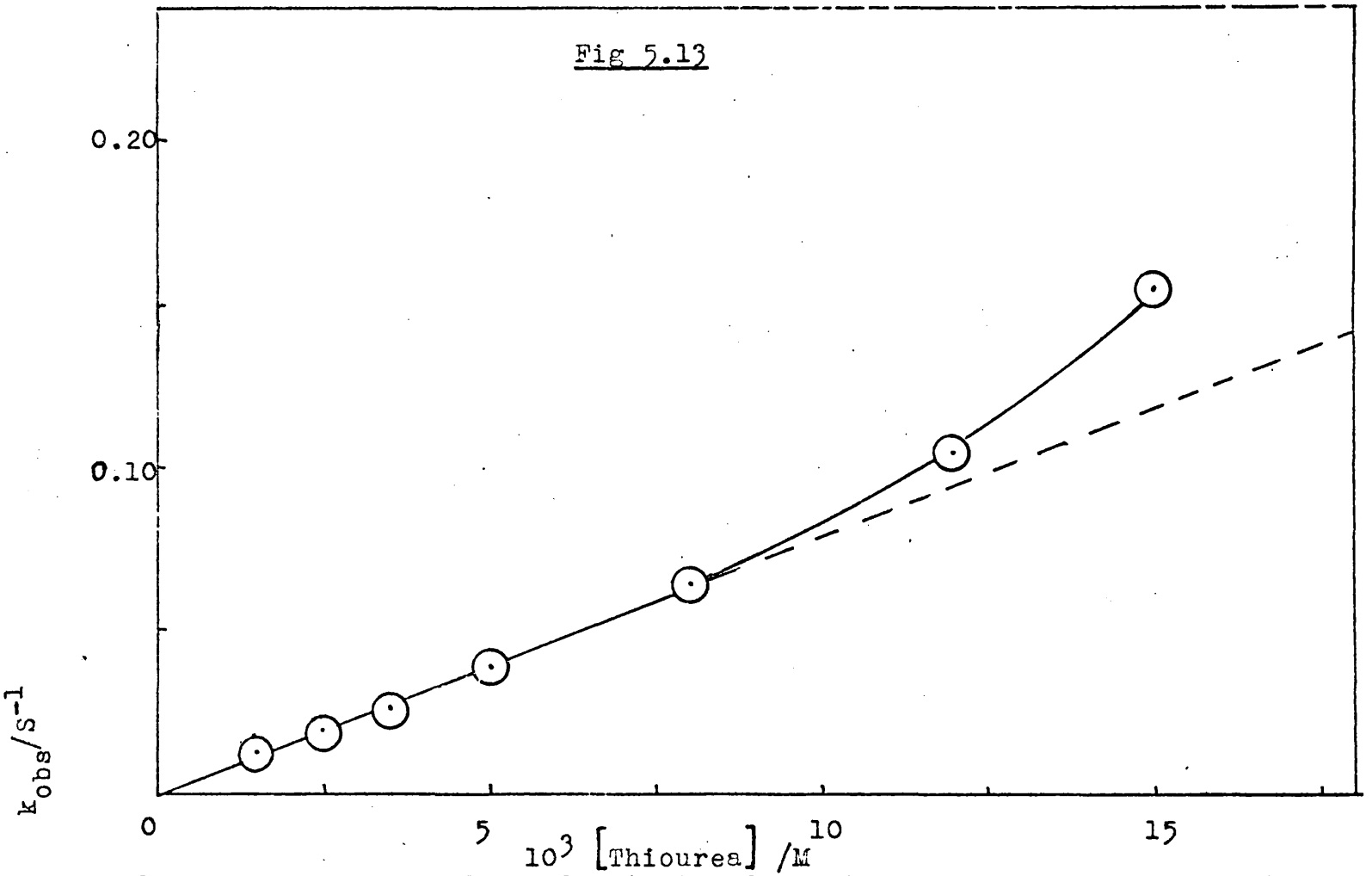
On plotting k_{obs} against ligand concentrations, interesting results were obtained. A first order dependence was observed for all the reactions up to a certain excess concentration of the ligand. At higher values a pronounced deviation was found (Figs 5.13 and 5.14). Plots of $\frac{k_{obs}}{[L]}$ versus $[L]$ were suggestive of a second path being second order in ligand concentrations (see figs 5.15 and 5.16). The

Fig 5.12

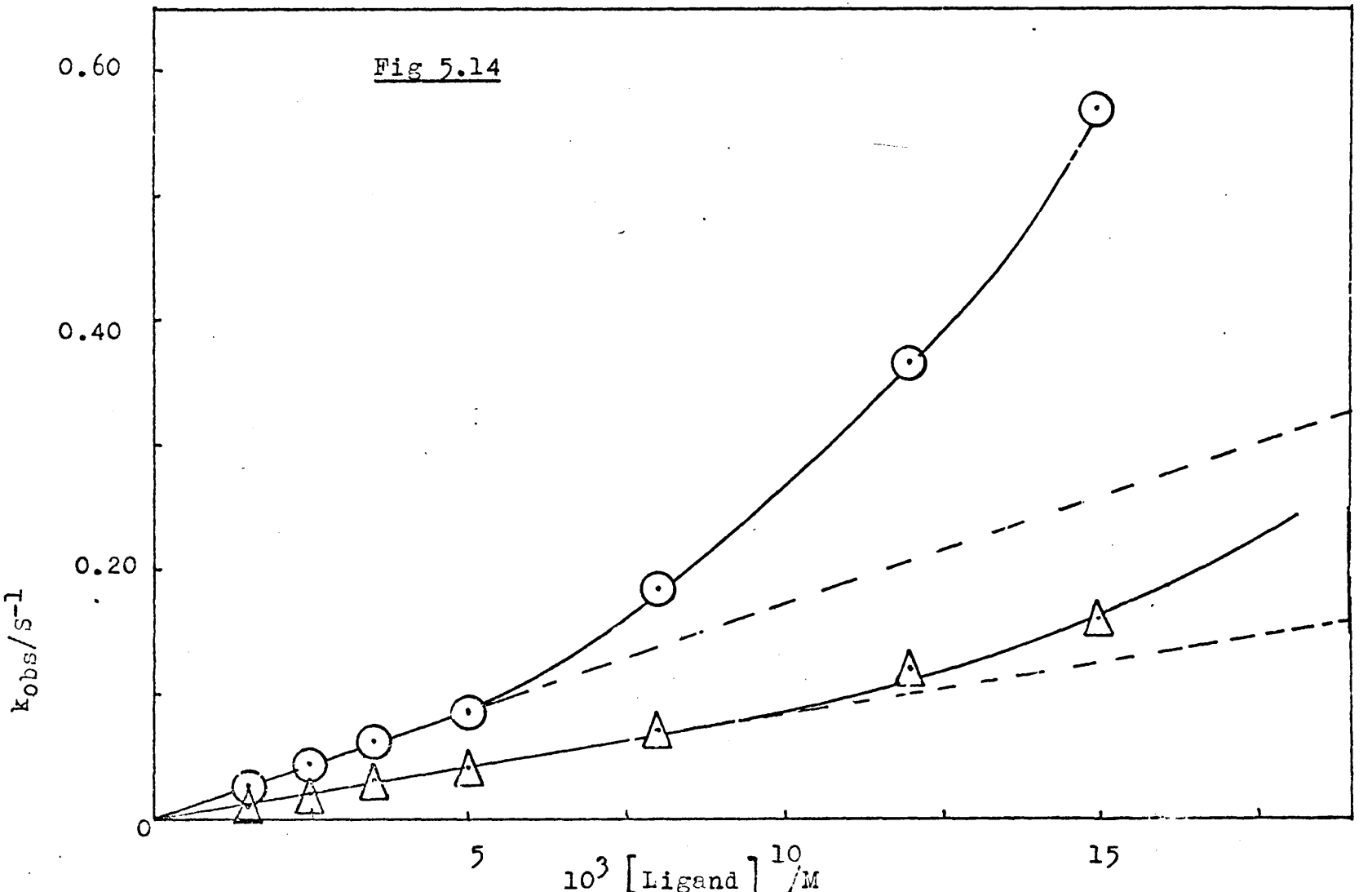


Plots of ln $(A_t - A_\infty)$ against time for the reduction of anion II by: (⊙) [Methylthiourea] 15 x 10^{-3} M at 35°C, $[H^+]$ = 1.0M; (△) [thiourea] 5 x 10^{-3}M at 25°C, $[H^+]$= 0.10M; and (□) [ethylenethiourea] 12 x 10^{-3}M at 8.7°C, $[H^+]$ = 1.0M.

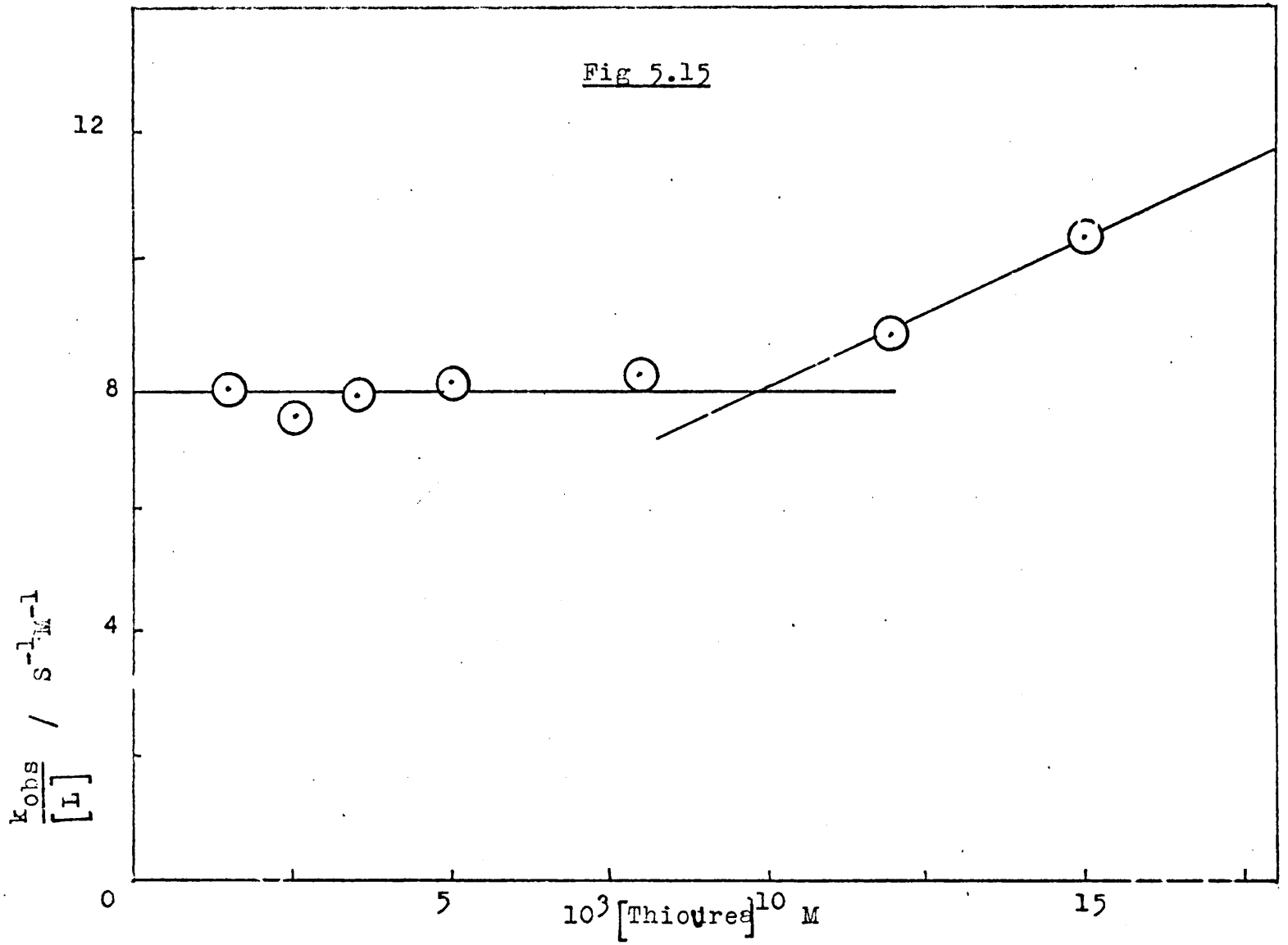
Fig 5.13



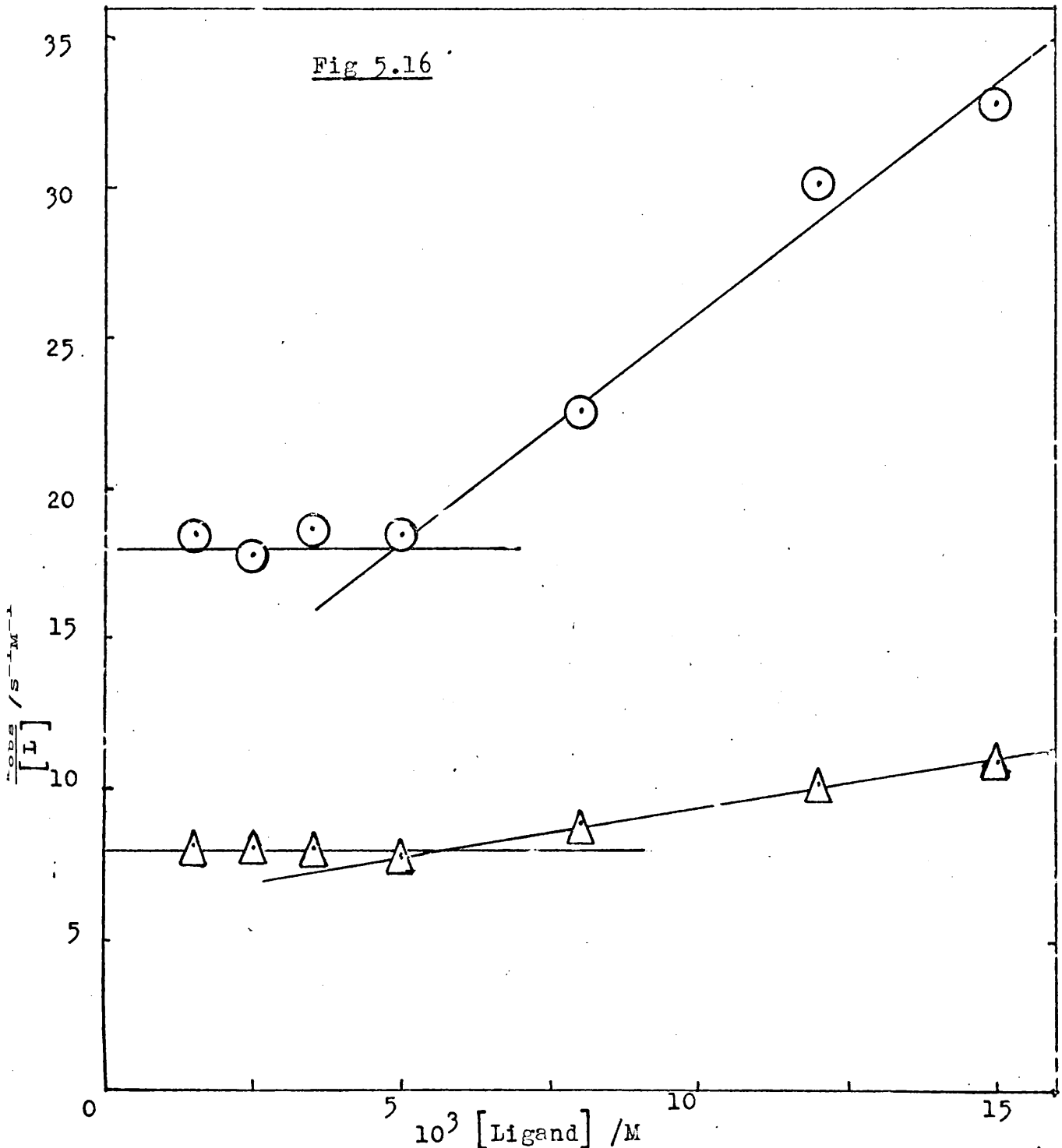
Ligand-dependence of pseudo-first-order rate constant for the reaction of anion II with thiourea at 25°C [Anion II] = 2 x 10^{-4}M, $[H^+]$ = 1.0M .



Ligand - dependence of pseudo-first-order rate constant for the reaction of anion II with (⊙) methylthiourea and (▲) ethylenethiourea. [Anion II] = 2 x 10^{-4}M, $[H^+]$ = 1.0M. at T= 25°C.



Plot of $\frac{k_{obs}}{[L]}$ against ligand for the reaction of anion II with thiourea at 25°C. $[H^+]$ = 1.0M [Anion II] = 2.10^{-4}M .



Plots of $\frac{k_{obs}}{[L]}$ against ligand for the reaction of anion II with (⊙) methylthiourea and (Δ) ethylenethiourea. [Anion II] = 2 x 10^{-4}M, $[H^+]$ = 1.0M and T = 25°C.

TABLE 5.1

Observed rate constants (k_{obs}) at varying ligand and hydrogen ion concentrations $[Co^{III}O_4W_{12}O_{36}]^{-5}$ = 2 x 10^{-4}M; I = 1.0M; λ = 390nm

L = Thiourea

Temp = 35°

$[H^+]_o$ = 1.0M

$[L]10^3$/M	k_{obs}/S^{-1}
1.5	0.0225
2.5	0.0365
3.5	0.0513
5.0	0.0752
8.0	0.134
12.0	0.202
15.0	0.260

$[H^+]$ = 0.50M

$[L]10$/M	k_{obs}/S^{-1}
1.5	0.0281
2.5	0.0358
3.5	0.04995
5.0	0.078
8.0	0.132
12.0	0.225
15.0	0.288

Temp = 25°C

$[H^+]$ = 1.0M

$[L]10^3$M	k_{obs}/S^{-1}
1.5	0.0119
2.5	0.0186
3.5	0.0268
5.0	0.040
8.0	0.0644
12.0	0.1040
15.0	0.1550
20	0.244

$[H^+]$ = 0.50M

$[L]10^3/M$	k_{obs}/S^{-1}
1.5	0.0121
2.5	0.0183
3.5	0.0259
5.0	0.044
8.0	0.0664
12.0	0.1052
15.0	0.164

$[H^+]$ = 0.10M

$[L]10^3/M$	k_{obs}/S^{-1}
5.0	0.0388
8.0	0.0689
12.0	0.109
20.0	0.25

Temp. = 18.6°C

$[H^+]$ = 1.0M

$[L]10^3/M$	k_{obs}/s^{-1}
1.5	0.0111
2.0	0.0175
2.5	0.0217
3.0	0.0264
3.5	0.0319
5.0	0.0413
8.0	0.0535

Temp. = 8.7°C

$[L]10^3/M$	k_{obs}/s^{-1}
1.5	0.0046
2.5	0.0080
3.5	0.0126
5.0	0.0180
8.0	0.033

L = NN^1-Ethylenethiourea

Temp = 35°C

$[H^+]$ = 1.0M

$[L]10^3$/M	k_{obs}/S^{-1}
1.5	0.0227
2.5	0.0367
3.5	0.0518
5.0	0.072
8.0	0.117
12.0	0.180
15.0	0.234

$[H^+]$ = 0.10M

$[L]10^3$/M	k_{obs}/S^{-1}
2.5	0.042
5.0	0.068
8.0	0.120

Temp = 25°C

$[H^+]$ = 1.0M

$[L]10^3$	k_{obs}/S^{-1}
1.5	0.0120
2.5	0.0215
3.5	0.0294
5.0	0.040
8.0	0.0696
12.0	0.117
15.0	0.154

$[H^+]$ = 0.10M

$[L]10^3$	k_{obs}/S^{-1}
1.5	0.0128
2.5	0.0227
3.5	0.0279
5.0	0.042

Temp = 18.6°C

$[H^+]$ = 1.0M

$[L]10^3/M$	k_{obs}/S^{-1}
1.5	0.0078
2.5	0.0123
3.5	0.0186
5.0	0.0245
8.0	0.0485

Temp = 8.7°C

$[H^+]$ = 1.0M

$[L]10^3/M$	k_{obs}/S^{-1}
1.5	0.0043
2.5	0.0073
3.5	0.0116
5.0	0.0173
8.0	0.0405

L = N-Methylthiourea

Temp = 35°C

$[H^+]$ = 1.0M		$[H^+]$ = 0.5M	
$[L]10^3$/M	k_{obs}/S^{-1}	$[L]10^3$/M	k_{obs}/S^{-1}
1.5	0.0493	1.5	0.0511
2.5	0.089	2.5	0.0799
5.0	0.169	5.0	0.159
8.0	0.294		
12.0	0.488		
15.0	0.628		

Temp = 25°C

$[H^+]$ = 1.0M

$[L]10^3$/M	k_{obs}/S^{-1}
1.5	0.0278
2.5	0.0446
3.5	0.0655
5.0	0.0925
8.0	0.1810
12.0	0.3620
15.0	0.5640

Temp = 18.6°C

$[H^+]$ = 1.0M

$[L]10^3/M$	k_{obs}/S^{-1}
1.734	0.0219
2.889	0.0427
4.045	0.0600
5.778	0.1251
9.246	0.3029

Temp = 8.7°C

$[H^+]$ = 1.0M

$[L]10^3/M$	k_{obs}/S^{-1}
1.5	0.0219
2.0	0.0289
2.5	0.0433
3.0	0.0729
4.0449	0.0924
5.778	0.1925
9.246	0.4442

range of the first-order dependence path was found to increase with increasing temperature, while the second - order path predominated at lower temperatures in all the reactions. A similar trend was also observed in the reactions of tris(1,10 - phenanthroline) iron(III) ion with the thioureas[151] and HSO_3^- ion.[152]

Representing $Co^{III}O_4W_{12}O_{36}^{-5}$ anion as Co^{III}, $Co^{II}O_4W_{12}O_{36}^{-5}$ anion as Co^{II} and the thioureas as RS, the following mechanisms can be postulated for the electron exchange reactions from both the stoicheiometric and kinetic data.

Mechanism I

$$Co^{III} + RS \xrightarrow{k_o} Co^{II} + RS^{\cdot} \qquad (5)$$

$$Co^{III} + RS \underset{}{\overset{K_{os}}{\rightleftharpoons}} Co^{III}\cdot RS \qquad (6)$$

$$Co^{III}\cdot RS \xrightarrow{k_1} Co^{II} + RS^{\cdot} \qquad (7)$$

$$Co^{III}\cdot RS + RS \xrightarrow{k_2} Co^{I} + RSSR \qquad (8)$$

$$Co^{I} + Co^{III} \rightleftharpoons 2Co^{II} \qquad (9)$$

$$2RS^{\cdot} \rightleftharpoons RSSR \qquad (10)$$

Mechanism II

Reactions (5), (6) and (7) above hold followed by:

$$Co^{III}.RS + RS \xrightarrow{k_2} Co^{II} + RSSR^{\bullet} \qquad (11)$$

$$RSSR^{\bullet} + Co^{III} \rightleftharpoons Co^{II} + RSSR \qquad (12)$$

$$2\,RS^{\bullet} \rightleftharpoons RSSR \qquad (10)$$

These reaction schemes are consistent with the rate of loss of anion II being expressed as in equation (13).

$$\frac{d[Co^{III}]}{dt} = \frac{k_0[Co^{III}][RS] + k_1K_{os}[Co^{III}][RS] + k_2K_{os}[Co^{III}][RS]^2}{1 + K_{os}[RS]} \qquad (13)$$

where K_{os} represents the outer - sphere equilibrium constant.

Assuming K_{os} to be of the order of unity the expression for the k_{obs} can be derived from equation (13).

$$k_{obs} = \left[k_0 + K_{os}\left\{(k_1 + k_2[RS])\right\}\right][RS] \qquad (14)$$

Re-arrangement of equation (14) gives equation (15).

$$\frac{k_{obs}}{[RS]} = k_0 + K_{os}k_1 + K_{os}k_2[RS] \qquad (15)$$

on plotting $\frac{k_{obs}}{[RS]}$ against $[RS]$,

However, two pathways were identified, one independent of and the other dependent on the ligand concentrations with the latter dominating at higher ligand concentrations and low temperatures (see Figs. 5.15 and 5.16). The observation is consistent with the proposed outer-sphere

mechanism in that the assumption made above of $K_{os}[RS] \ll 1$ may not hold at higher ligand concentrations which would explain the curvature obtained in this region in the plots of k_{obs} versus [RS] (Figs. 5.13 and 5.14). It would also explain the temperature dependence of this second-order path since the thermodynamic parameter K_{os} is expected to be higher at low temperatures, again making the $K_{os}[RS] \ll 1$ assumption untenable.

A curve fitting method was adopted to evaluate the various rate constants using a computer programme shown in Appendix II. However inconsistent values were obtained for k_1 and k_2 whereas a constant value to ± 5% was obtained for k_o in each case at constant temperature. These k_o values are in agreement with those obtained from the slopes of the plots of k_{obs} against [RS] and also from the initial part of the plots of $k_{obs}/[RS]$ versus [RS]. This suggests that the k_o pathway is the dominant one at concentration of ligand up to ~ 20% excess. The values of k_o so obtained at different temperatures are presented in Table 5.2. It would therefore seem that it is only at very low ligand concentrations that the mechanism of these reactions can be considered as being more readily established.

A similar outer-sphere mechanism to those above, has been postulated by Carlyle for the reaction of HSO_3^- with tris - (1,10 - phenanthroline) iron (III)[152] ion and the

TABLE 5.2

Variation of the rate constants k_o (equation 6) with temperature.

L = Thiourea

Temperature/°C	k_o/l mol^{-1}S^{-1}
8.7	3.44
18.6	7.00
25.0	7.96
35.0	14.2

ΔH^* = 9.7±0.3 K cal mol^{-1}; ΔS^* = -21.7±2cal K^{-1} mol^{-1}

L = NN^1-Ethylenethiourea

Temperature/°C	k_o/l mol^{-1}S^{-1}
8.7	2.90
18.6	5.24
25.0	8.10
35.0	14.50

ΔH^* = 9.9±0.4 K cal mol^{-1}; ΔS^* = -21.0±2 cal K^{-1}mol^{-1}

L = N- Methylthiourea

Temperature/°C	k_o/ l mol^{-1} S^{-1}
18.6	12.0
25.0	18.0
35.0	34.0

ΔH = 12.0 ∓1 K Cal mol^{-1}; ΔS = −11·8 ± 3 Cal K^{-1} mol^{-1}

activation parameters for reaction (5) in these studies (Table 5.2) are similar in magnitude with those obtained for the $Fe(phen)^{3+}$ + L pathway. However the alternative mechanism put forward by the same author involving dimerisation of the ligand as the first step followed by a rate - determining two electron-transfer reaction is not deemed feasible in the present investigations because of the kinetic inertness of the disulphide product.

Although it is difficult to say precisely whether the complex formed is outer - sphere, the absence of any detectable intermediate coupled with the structure[155,158] and stability[159] of anions I and II would make this a real possibility.

A third mechanism which also gives a 1:1 stoicheiometry is given below

$$Co^{III} + RS \xrightarrow{k_o} Co^{II} + RS^{\bullet} \qquad (5)$$

$$RS^{\bullet} + RS \underset{1}{\rightleftharpoons} RSSR^{\bullet} \qquad (16)$$

$$Co^{III} + RSSR^{\bullet} \xrightarrow{k_2} Co^{II} + RSSR \qquad (17)$$

$$2RS^{\bullet} \rightleftharpoons RSSR \qquad (10)$$

If this mechanism was operating, it would be difficult to explain the temperature dependence of the second-order path without invoking an outer-sphere complex formation of some sort. Mechanism I postulated earlier for these reactions is not likely to be operating either because the addition of up to 0.015M $[Co(en)_2Cl_2]^+$ to reacting solutions of anion II and the ligand had no effect on both the

stoicheiometry and the rate of these reactions. This would not be the case if Co^{I} is an important intermediate. Mechanism II therefore seems to be the most favoured.

Since only very few kinetic studies of the reactions of $[Co^{III}O_4W_{12}O_{36}]^{-5}$ anion has so far been investigated more work is required in the following areas to establish beyond doubt the nature of the oxidation reactions involving this oxidant.

a) A reliable method for characterising and possibly distinguishing between the radicals formed by the ligand and those by the dimeric species of the ligand would clear some of these uncertainties.

b) A full investigation of the medium effects in these reactions may also prove useful.

c) A study of the trace metal ion catalysis for these systems might throw some light on the mechanisms of the reactions.

d) It is also of interest to see what the rate law would be if these reactions are carried out under excess complex anion II where no second-order dependence on the ligand concentrations is expected.

e) Finally, a second-order pathway has been established for the reactions of $Fe(phen)_3^{3+}$ with HSO_3^- (ref 152) and also for those of chromium (VI) with some sulphur - containing ligands referred to in the preceding chapters. Investigation of the reactions of the complex anion II with other non - sulphur

containing ligands like iodide ions and hydroquinone might help in establishing whether this second - order pathway is merely a feature of sulphur chemistry.

A P P E N D I X I

Computer programme (in extended basic) used to calculate the absorbance changes occurring in the course of a reaction and also values for log $(OD_{\infty} - OD_t)$ and k_{obs}

```
*NEW
*
*ØØØ1 PRINT "  GAIN          B.O.          R.B.O.        R.I."
*ØØØ4 LET C7=1
*ØØØ7 INPUT A1;
*ØØØ8 LET A1=1.Ø32*A1
*ØØ1Ø PRINT ,;
*ØØ13 INPUT A2;
*ØØ16 PRINT ,;
*ØØ19 INPUT A3;
*ØØ"" PRINT ,;
*ØØ25 INPUT A4
*ØØ28 PRINT "TIME",;
*ØØ31 INPUT A5
*ØØ34 LET A5=A5/2
*ØØ37 PRINT "  R.O.T.        TIME          O.D.          LN(O.D.)"
*ØØ4Ø GOTO ØØ46
*0043 LET D6=B2
*ØØ46 INPUT A6;
*ØØ49 IF A6=999THEN GO TO Ø154
*ØØ52 LET A7=(A2*.ØØ5575)-(A1=A3)
*ØØ55 LET A8=A8+1
*ØØ58 LET A9=A7+(A6*A1)
*ØØ61 LET B1=A7+(A4*A1)
*ØØ64 LET B2=(LOG(A9)-LOG(B1))/2.3Ø3
*ØØ67 LET B2=ABS(B2)
*ØØ7Ø LET B3=LOG(B2)
*ØØ73 LET B4=A8*A5
*ØØ76 PRINT,B4,;B2,;B3,;
*ØØ79 PRINT ""
*ØØ82 LET B5=B5+1
*ØØ85 IF B5=1THEN GOTO ØØ43
*ØØ88 IF B5=2THEN GO TO ØØ46
*ØØ91 IF B5=3THEN GO TO Ø1ØØ
*ØØ94 GO TO Ø118
*ØØ97 PRINT ""
*Ø1ØØ LET B6=B4
*Ø1Ø3 LET B7=B6*B6
*Ø1Ø6 LET B8=B3
*Ø1Ø9 LET B9=B8*B8
*Ø112 LET C1=B6*B8
*Ø115 GO TO ØØ46
*Ø118 LET C2=B4
```

```
*Ø121 LET B6=B6+O2
*Ø124 LET C3=C2*C2
*Ø127 LET B7=B7+C3
*Ø13Ø LET C4=B3
*Ø133 LET B8=B8+C4
*Ø136 LET C5=C4*C4
*Ø139 LET B9=B9+C5
*Ø142 LET C6=C4*C2
*Ø145 LET C1=C1*C6
*Ø148 LET C7=C7+1
*Ø151 GO TO ØØ46
*Ø154 LET C9=B6*B6
*Ø157 PRINT ""
*Ø16Ø PRINT,B6;,B7;,C1;,
*Ø163 PRINT ""
*Ø157 PRINT ""                    7;,
*Ø16Ø PRINT,B6;,B7;,C1;,
*Ø163 PRINT ""                    C1))/(C9-(C7*B7))
*O166 PRINT, B8;,B9;,B9;.C7;,B7))/CC9-(C7*B7))
*Ø169 PRINT ""                    -(2*D1*B8)+(2*C8*D1*B6)+(B7*C8+2)+(C7*D1
                                                                  +2))
*Ø181 LET D2=D2/¢C7-2)
*Ø184 LET D3=(C7*B7)-B6+2
*Ø157 LET D4=C7*D2/D3
*Ø19Ø LET D5=B7*D2/D3
*Ø193 LET D2=SQR(ABS(D2))
*Ø196 LET D4=SQR(ABS(D4))
*Ø199 LET D5=SQR(ABS(D5))
*Ø2Ø2 PRINT ""
*Ø2Ø5 PRINT "GRADIENT & ERROR",C8,D4
*Ø2Ø6 PRINT ""
*Ø211 PRINT "INTERCEPT & ERROR", D1,D5
*Ø214 PRINT ""
*Ø217 PRINT "ROOT MEAN SQR ERROR", D2
*Ø22Ø LET D7=Ø25
*Ø223 LET D8=D6*EXP(ABS(C8)*D7)
*Ø226 LET D9=(D8-D6)/D7
*Ø229 PRINT ""
*Ø232 PRINT "O.D.Ø. & INIT. RATE.", D8,D9
*Ø235 END
*
**
```

A P P E N D I X II

Computer programme (in extended Basic) used to evaluate the rate constants k_0, k_1 and k_2 for the reactions of $Co^{III}O_4W_{12}O_{36}^{-5}$ with the thioureas.

```
ØØØ1 PRINT "K1"
ØØØ2 INPUT K
ØØØ3 PRINT "L1"
ØØØ4 INPUT L
ØØØ5 PRINT "K2"
ØØØ6 INPUT O
ØØØ7 PRINT "L2"
ØØØ8 INPUT P
ØØØ9 PRINT "K3"
ØØ1Ø INPUT S
ØØ11 PRINT "L3"
ØØ12 INPUT T
ØØ13 LET M=K*L
ØØ14 LET N=L+2
ØØ15 LET Q=O*P
ØØ16 LET R=P+2
ØØ17 LET U=S*T
ØØ18 LET V=T+2
ØØ19 LET D=(P*K-O*L)*(P*U-T*Q)
ØØ2Ø LET E=(P*S-T*O)*(P*M-L*Q)
```

```
ØØ21 LET F=(P*N-L*R)*(P*U-T*Q)
ØØ22 LET G=(P*V-T*R)*(P*M-L*Q)
ØØ23 LET C=(D-E)/(F-G)
ØØ24 LET B=((P*K-O*L)-(P*N*C-L*R*C))/(P*M-L*Q)
ØØ25 LET A=(K-B*M-C*N)/L
ØØ26 PRINT A,B,C
ØØ27 GO TO ØØØ1
```

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